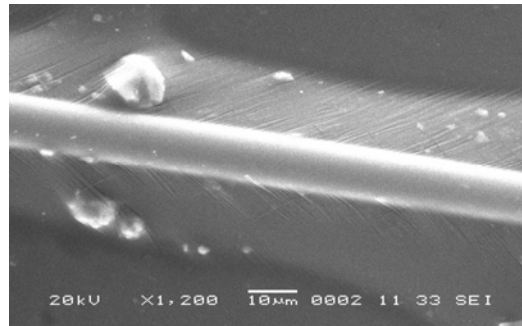


ASSESSMENT OF SMALL INTERACTIONS AND STRUCTURAL GRADIENT AT THE INTERFACE OF FRP COMPOSITES BY FTIR-IMAGING AND DSC TECHNIQUES



A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

Master of Technology
in
Metallurgical and Materials Engineering

By
Neeti



Department of Metallurgical and Materials Engineering
National Institute of Technology
Rourkela
2007

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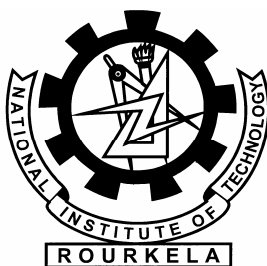
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2007



**National Institute of Technology
Rourkela**

CERTIFICATE

This is to certify that the thesis entitled, “**Assessment of small interactions and structural gradient at the interface of FRP composites by FTIR-imaging and DSC techniques**” submitted by Ms **Neeti** in partial fulfillment of the requirements for the award of Master of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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N.I.T. Rourkela

(Neeti)

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ABSTRACT

Environmental degradation of FRP composite was studied. The degradation study basically included hygrothermal and cryogenic treatment. Study of chemical and mechanical behaviour at the interface of the fibre reinforced polymer composites is an area of research now a day. Many complex reactions occur at the interface due to moisture absorption, temperature and cryogenic treatment and very little information is available regarding the chemical deviation near the interface due to moisture absorption. Micro-composites were prepared to investigate the chemical deviation of hygrothermally samples and layered structures were prepared to study the mechanical behaviour of cryogenically treated samples.

The present work used FTIR-imaging and modulated temperature DSC to assess the structural gradient at the interface due to hygrothermal ageing of glass/epoxy and glass/polyester composite materials. The specimens were conditioned at 50°C in hydrothermal chamber with 95% humidity for the varying degree of duration i.e. 10- 50 hours. The samples were compared before and after the hydrothermal aging near the interface i.e. in the interphase region to evaluate the chemical changes from the bulk of the matrix phase by FTIR-imaging. The degree of curing also varies in going from away from the interface into the bulk of the matrix phase. DSC was also done to study the deviation in the glass transition temperature of FRP composites. Mechanical properties of composite materials are dependent on the properties of the interphase region and even small chemical deviation effect the overall performance of composite materials. It was observed that hygrothermal treatment leads to change in chemical spectra and glass transition temperature near the interface which ultimately leads to change in interface dominating properties.

Another experimental investigation deals with the mechanical behaviour of glass/epoxy composites at cryogenic temperature. Woven and chopped E-glass fibres of 50 weight percentage were reinforced with epoxy matrix to prepare the laminated composites. 3 point bend tests were carried out to assess interlaminar fracture behaviour at cryogenic and at ambient conditions. The specimens were tested at a range of 2 mm/min to 500 mm/min crosshead speed to evaluate the sensitivity of mechanical response during loading at these conditions. The mechanical performances of the laminated specimens at cryogenic conditions were compared with room temperature property by using SEM photographs. DSC test was carried out to study

whether there is any change in glass transition temperature and chemical structure after cryogenic treatment. Glass/epoxy composites were found to be loading rate sensitive. DSC analysis shows increase in glass transition temperature after cryogenic conditioning which may be due to irreversibility of the chain mobility. Phenomenological behaviour of these composite materials may be attributed by polymer relaxation at low temperature, cryogenic hardening, matrix cracking, and misfit strain due to differential thermal coefficient of the fibre and the matrix and also by enhanced mechanical keying factor by compressive residual stresses generated at cryogenic temperatures.

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1. INTRODUCTION

1.1 Background

Although the concept of fibre reinforced materials can be traced back to the use of straw as reinforcement in bricks manufactured by the Isrealites in 800 B.C., and in more recent times to the use of short glass fiber reinforcement in cement in the United States in the early 1930's, fiber reinforced resin matrix materials (or fibre reinforced composites as we know them today) were not developed until the early 1940's. In this work the term composites are used in the context of advanced fibre reinforced polymers (FRP's).

After World War II, US manufacturers began producing fibre glass and polyester resin composite boat hulls and radomes (radar cover). The automotive industry first introduced composites into vehicle bodies in the early 1950s. Because of the highly desirable light weight, corrosion resistance, and high strength characteristics in composites; research emphasis went into improving the material science and manufacturing process. That effort led to the development of two new manufacturing techniques known as filament winding and pultrusion, which helped advance the composite technology into new markets. There was a great demand by the recreation industry for composite fishing rods, tennis rackets, ski equipment and golf clubs. The aerospace industry began to use composites in pressure vessels, containers, and non-structural aircraft components. The US Navy applied composites in mine sweeping vessels, crew boats and submarine parts. The domestic consumers began installing composite bath tubs, covers, railings, ladders and electrical equipment. The first civil application in composites was a dome structure built in Benghazi in 1968, and other structures followed slowly.

The Composites Institute, that tracks the domestic economy, reported the total consumption figures for 1994 and 1995 at more than three billion pounds each year. Of the nine industries reported, the transportation industry claimed 31% of the total market, thus, being the biggest consumer of composites in both years. The preliminary figure for 1994 was 945.6 million pounds followed by 1995 with 984 million pounds. It is predicted that orders for composites in the transportation sector will exceed one billion pounds for 1996.

With the increasing demand for composites, new and improved manufacturing processes such as pultrusion, resin transfer molding, and filament winding were developed and implemented in the early 1990s. With these enhancements in place, the current focus is to rebuild the US transportation infrastructure using FRP composites for maintenance and rehabilitation of existing bridges as well as new construction.

Composites are class of materials is characterized by the marriage of quite diverse individual components that work together to produce capabilities exceeds those of their separate elements. In broad sense composites are materials consist of two or more constituents. The constituents are combined in such a way that they keep their individual physical phases and are not soluble in each other or not to form a new chemical compound. One constituent is called reinforcing phase and the one in which the reinforcing phase is embedded is called matrix.

A fiber-reinforced composite is not simply a mass of fibres dispersed within a polymer, metal, or ceramic matrix. A composite consists of fibres embedded in or bonded to a matrix with distinct interfaces (or interphases) between the two constituent phases. The fibres are usually of high strength and modulus and serves as the principal load carrying members. The matrix must keep the fibres in a desired location and orientation, separating fibres in a desired location and orientation, separating fibres from each other to avoid mutual abrasion during periodic straining of the composite. The matrix acts as a load transfer medium between fibres, and in less ideal cases where loads are complex, the matrix may even have to bear loads transverse to the fibres axis. Since the matrix is generally more ductile than the fibres, it is the source of composite toughness. The matrix also serves to protect the fibres and the matrix largely retains their identities and yet results in many properties that cannot be achieved with either of the constituents acting alone.

A great majority of material are stronger and stiffer in the fibrous form than as a bulk material. A high fibre aspect ratio (length to diameter ratio) permits very effective transfer of load via matrix materials to the fibers, thus taking advantage of their excellent properties. Therefore, fibres are very effective attractive reinforcement materials.

The fibre is an important constituent in composites. A great deal of research and development has been done with the fibres on the effects in the types, volume fraction, architecture, and orientations. The fiber generally occupies 30% - 70% of the matrix volume in the composites. The fibres can be chopped, woven, stitched, and/or braided. They are usually treated with sizing such as starch, gelatin, oil or wax to improve the bond as well as binders to

improve the handling. The most common types of fibres used in advanced composites for structural applications are the fibre glass, aramid, and carbon. The fibre glass is the least expensive and carbon being the most expensive. The cost of aramid fibres is about the same as the lower grades of the carbon fibre. "Other high-strength high-modulus fibres such as boron are at the present time considered to be economically prohibitive.

Many of our modern technology require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics and polymeric materials. This is especially true for materials that are needed for aerospace, under water and transportation applications. For example aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff and abrasion and impact resistance, and are not easily corroded. This is a rather formidable combination of characteristics. Frequently, strong materials are relatively dense; also, increasing the strength or stiffness generally results in a decrease in impact strength [1].

Various advantages of composite materials are its high specific stiffness (E/ρ) and high specific strength (σ_{ult}/ρ). These properties are generally used in structural application such as aerospace and sporting goods [2].

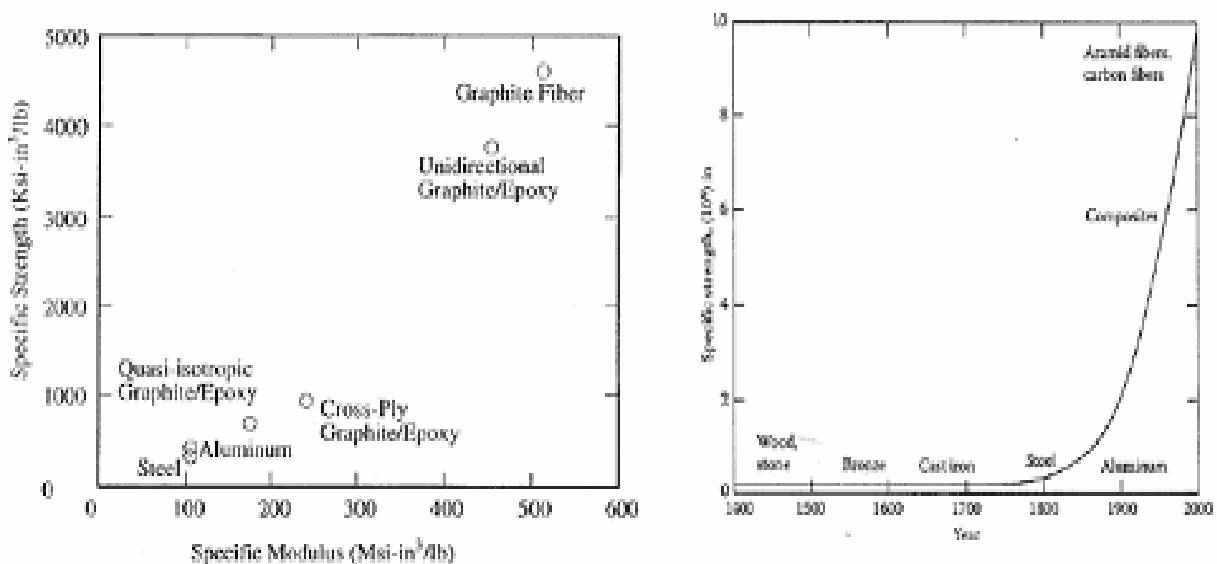


Fig.1.1. Specific strength versus specific modulus and Year.

1.2. Composites offer many advantages over other materials. The many advantages of composites may be summarized as:

1.2.1. Stronger and stiffer than metals on a density basis

For the same strength, lighter than steel by 80% and aluminum by 60%

Superior stiffness-to-weight ratios

1.2.2. Capable of high continuous operating

1.2.3. Highly corrosion resistant:

Essentially inert in the most corrosive environments

Electrically insulating properties are inherent in most composites (depending on reinforcement selected).

Yet composites can be made conducting or selectively conducting as needed.

1.2.4. Tailorable thermal expansion properties

Can be compounded to closely match surrounding structures to minimize thermal stresses

1.2.5. Exceptional formability

Composites can be formed into many complex shapes during fabrication, even providing finished, styled surfaces in the process.

1.2.6. Outstanding durability

Well-designed composites have exhibited apparent infinite life characteristics, even in extremely harsh environments

1.2.7. Low investment in fabrication equipment

The inherent characteristics of composites typically allow production to be established for a small fraction of the cost that would be required in metallic fabrication.

1.2.8. Reduced Part Counts

Parts that were formerly assembled out of several smaller metallic components can be fabricated into a larger single part. This reduces manufacturing and assembly labor and time.

1.2.9. Corrosion Resistance

The non-reactive nature of many resins and reinforcements can be custom selected to resist degradation by many common materials and in corrosive environments.

Benefits include lower maintenance and replacement costs.

1.3. Fibre Reinforced Polymer (FRP) Composites

The most common advanced composites are fibre reinforced polymeric composites. These composites consist of a polymer matrix reinforced with high performance thin-diameter fibres. The reasons why they are the most common composites include low cost, high strength and simple manufacturing principles. The drawbacks of FRP composites are low operating temperature, high coefficient of thermal and moisture expansion, and low elastic properties in transverse direction. The typical mechanical properties of some common FRP composites and metals are given in the following table.

Table1.1. Typical Mechanical Properties of FRP and Metals

Properties	Graphite/epoxy ($V_f=0.7$)		Glass/ epoxy ($V_f=0.45$)		Steel	Aluminum
	Longi- tudinal	Trans- verse	Longi- tudinal	Trans- verse		
Specific gravity (g/cm^3)	1.6	1.6	1.8	1.8	7.8	2.6
Young's Modulus (GPa)	181	10.3	38.6	8.27	206	68.9
Ultimate Tensile Strength (MPa)	1500	40	1062	31	648	276
Coefficient of thermal expansion ($\mu\text{m/m}^\circ\text{C}$)	0.02 5	22.	8.6	22.1	11.7	23

Table 1.2. Typical Mechanical Properties of Fibres and Metals

Properties	Graphite	Glass	Aramid (Kevlar)	Steel	Aluminum
Specific gravity (g/cm ³)	1.8	2.5	1.4	7.8	2.6
Young's Modulus (GPa)	230	85	124	206	68.9
Ultimate Tensile Strength (MPa)	2067	1550	1379	648	276
Coefficient of thermal expansion (μm/m ⁰ C)	-1.3	5	-5	11.7	23

1.4. Reinforcement materials

A great majority of materials are stronger and stiffer in fibrous form than as bulk materials. A high fibre aspect ratio (length: diameter ratio) permits very effective transfer of load via matrix materials to the fibres, thus taking advantage of their excellent properties. Therefore, fibres are very effective and attractive reinforcement materials.

Types of fibers used in fibre reinforced polymer composites

1.4.1. Glass fibres

1.4.2. Carbon fibres

1.4.3. Aramid fibres

1.4.1. Glass fibres

The most common reinforcement for the polymer matrix composites is a glass fibre. Most of the fibres are based on silica (SiO_2), with addition of oxides of Ca, B, Na, Fe, and Al. The glass fibres are divided into three classes -- E-glass, S-glass and C-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C-glass is for high corrosion resistance, and it is uncommon for civil engineering application. Of the three fibres, the E-glass is the most common reinforcement material used in civil structures. It is produced from lime-alumina-borosilicate which can be easily obtained from abundance of raw materials like sand. The glass fibre strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily. The fibre itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

- **E-glass (electrical)**

Family of glasses with a calcium aluminum borosilicate composition and a maximum alkali composition of 2%. These are used when strength and high electrical resistivity are required.

- **S-glass (tensile strength)**

Fibres have a magnesium alumino-silicate composition, which demonstrates high strength and used in application where very high tensile strength required.

- **C-glass (chemical)**

It has a soda lime borosilicate composition that is used for its chemical stability in corrosive environment. It is often used on composites that contain or contact acidic materials [3].

Table 1.3. Composition of E-Glass

Constituent	Weight percentage
SiO_2	54
Al_2O_3	14
$\text{CaO}+\text{MgO}$	12
B_2O_3	10
$\text{Na}_2\text{O}+\text{K}_2\text{O}$	Less than 2
Impurities	Traces

Table1.4. Comparison of properties of Glass Fibre

Typical Properties	E-Glass	S-Glass
Density (g/cm ³)	2.60	2.50
Young's Modulus (GPa)	72	87
Tensile Strength (GPa)	1.72	2.53
Tensile Elongation (%)	2.4	2.9

1.4.1.1. Structure of glass fibre

Glass fibres have high tensile strength, impact strengths and high chemical resistance. But these have relatively low modulus, self-abrasiveness, low fatigue resistance and poor adhesion to matrix composites.

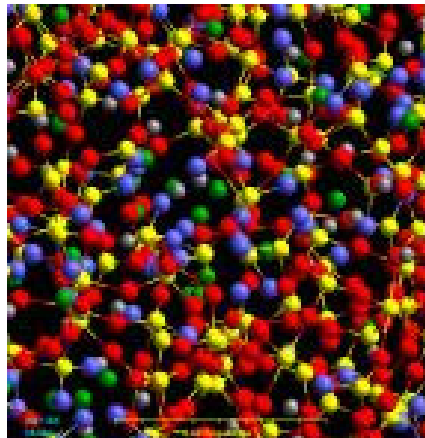


Fig.1.2. Polyhedra network structure of glass [4]

The three dimensional network of structure of glass results in isotropic properties of glass fibres, in contrast to those of carbon and Kevlar aramid fibres which are anisotropic. The elastic modulus of glass fibres measured along the fibre axis is the same as that measured in the transverse direction, a characteristic unique to glass fibres.

1.4.1.2. Surface Treatment of Reinforcing Materials

Surface treatment is done to improve the adhesion of fillers and fibres to matrix resin by modifying the surface of the solid. Often, chemical structure and sometimes topology of the surface change upon the treatment.

Chemistry of Surface Treatment and Interfacial Structure

Glass Fibres and Inorganic Fillers

Inorganic materials like glass fibres and many fillers have poor compatibility at the fibre/matrix or filler/matrix interface. In order to improve adhesion at the interface, compounds with dual property, i.e. molecules having chemical functionalities similar to the fibre and the matrix resin, are used. Due to the coupling action of the fibre and the resin by the compatibilizing compound, this type of compound is often referred to as a coupling agent, such as a silane coupling agent. In addition to the adhesion promotion, coupling agents aid in protecting fibre surfaces and prevent inhibition of polymerization by the solid surfaces. A small amount of a coupling agent can often dramatically improve the mechanical and physical properties of composites. A typical loading level of coupling agent ranges from a small fraction of a percent to a few percent based on the weight of the fibre or filler. Other treatments such as plasma and corona discharge changes the chemical structure of the surface layers of fillers and fibers in an attempt to obtain similar compatibilization and adhesion promotion effects through chemical reactions.

The coupling agent may be added to the filler as a neat liquid, an organic solution, or an aqueous solution. If a coupling agent is mixed into the filler/resin mixture, the treatment is called the integral blending method. On the other hand, if filler is separately treated, it is either termed as the dry blending method or the slurry treatment method. The dry blending method utilizes typically a small amount of a concentrated silane/organic solvent solution which is sprayed onto the tumbling fillers. Since the amount of the solution is small, and is an organic solution, the tumbling filler has an appearance of dry powder, thus the name dry blending method. The slurry method uses a large amount of a dilute silane solution, typically of an aqueous solution, and the filler is suspended in a slurry form.

The chemical reaction of a coupling agent occurring during the treatment and drying of the filler is shown below using a silane coupling agent for example [5].

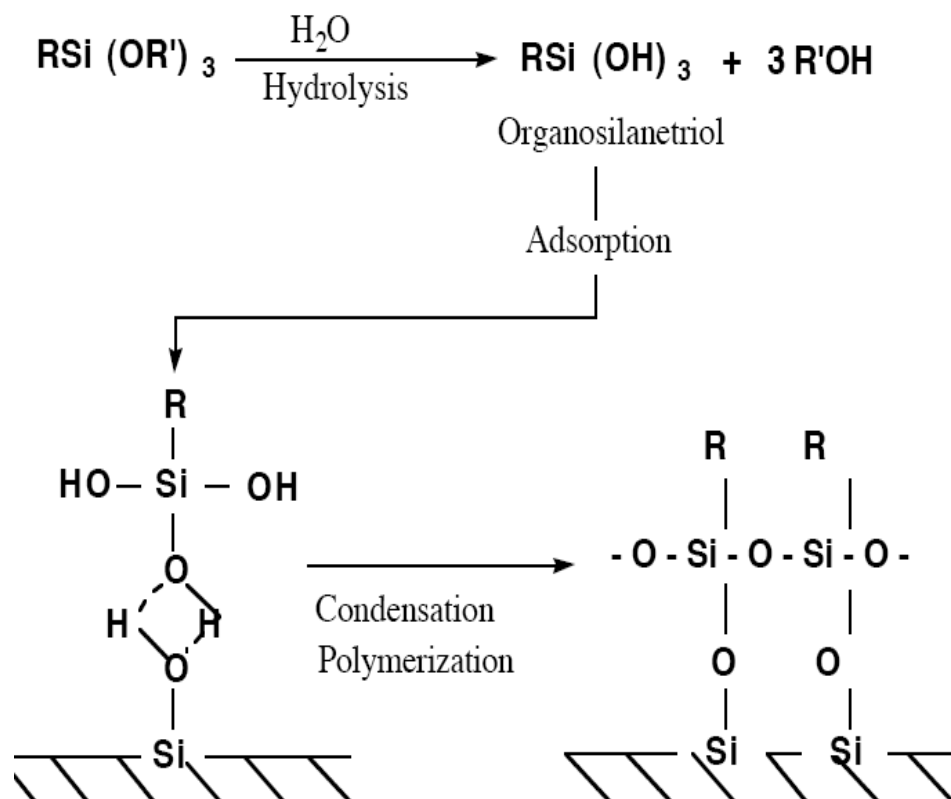


Fig.1.3. Chemical process during surface treatment silaceous material by a silane coupling agent.

Regardless of the treatment methods, the silane loses its alkoxy groups and chemically reacts with the hydroxyl groups of the mineral surfaces.

1.4.2. Carbon fibres

Carbon fibre is the most expensive of the more common reinforcements, but in space applications the combination of excellent performance characteristics coupled with light weight make it indispensable reinforcement with cost being of secondary importance. Carbon fibres consist of small crystallite of turbostratic graphite. These resemble graphite single crystals except that the layer planes are not packed in a regular fashion along the c-axis direction. In a graphite single crystal the carbon atoms in a basal plane are arranged in hexagonal arrays and held together by strong covalent bonds. Between the basal planes only weak Van-der-waal forces exist. Therefore the single crystals are highly anisotropic with the plane moduli of the order of 100 GPa whereas the molecules perpendicular to the basal plane are only about 75 GPa. It is thus evident that to produce high modulus and high strength fibres, the basal planes of the graphite

must be parallel to the fibre axis. They have lower thermal expansion coefficients than both the glass and aramid fibres. The carbon fibre is an anisotropic material, and its transverse modulus is an order of magnitude less than its longitudinal modulus. The material has a very high fatigue and creep resistance. Since its tensile strength decreases with increasing modulus, its strain at rupture will also be much lower. Because of the material brittleness at higher modulus, it becomes critical in joint and connection details, which can have high stress concentrations. As a result of this phenomenon, carbon composite laminates are more effective with adhesive bonding that eliminates mechanical fasteners [6].

Table 1.5. Typical properties of Carbon Fibre

Typical Properties	Density (g/cm ³)	Young's Modulus (GPa)	Tensile Strength (GPa)	Tensile Elongation (%)
High Strength	1.8	230	2.48	1.1
High Modulus	1.9	370	1.79	0.5
Ultra-High Modulus	2.0 - 2.1	520 – 620	1.03 - 1.31	0.2

1.4.3. Kevlar fibres

Kevlar (poly-paraphenylene terephthalamide) is the DuPont Company's brand name for a synthetic material constructed of para-aramid fibres that the company claims is five times stronger than the same weight of steel, while being lightweight, flexible and comfortable. It is also very heat resistant and decomposes above 400 °C without melting. It was invented by Stephanie Kwolek of DuPont from research into high performance polymers, and patented by her in 1966 and first marketed in 1971. Kevlar is a registered trademark of E.I. du Pont de Nemours and Company [1].

Originally intended to replace the steel belts in tires, it is probably the most well known name in soft armor (bulletproof vests). It is also used in extreme sports equipment, high-tension drumhead applications, animal handling protection, composite aircraft construction, fire suits, yacht sails, and as an asbestos replacement. When this polymer is spun in the same way that a spider spins a web, the resulting commercial para-aramid fibre has tremendous strength, and is

heat and cut resistant. Para-aramid fibres do not rust or corrode, and their strength is unaffected by immersion in water. When woven together, they form a good material for mooring lines and other underwater objects. However, unless specially waterproofed, para-aramid fibre's ability to stop bullets and other projectiles is degraded when wet. Kevlar is a type of aramid that consists of long polymeric chains with a parallel orientation. Kevlar derives its strength from inter-molecular hydrogen bonds and aromatic stacking interactions between aromatic groups in neighboring strands. These interactions are much stronger than the Van der Waals interaction found in other synthetic polymers and fibres like Dyneema. The presence of salts and certain other impurities, especially calcium, would interfere with the strand interactions and has to be avoided in the production process. Kevlar consists of relatively rigid molecules, which form a planar sheet-like structure similar to silk protein.

These properties result in its high mechanical strength and its remarkable heat resistance. Because it is highly unsaturated, i.e. the ratio of carbon to hydrogen atoms is quite high, it has a low flammability. Kevlar molecules have polar groups accessible for hydrogen bonding. Water that enters the interior of the fibre can take the place of bonding between molecules and reduce the material's strength, while the available groups at the surface lead to good wetting properties. This is important for bonding the fibres to other types of polymer, forming a fibre reinforced plastic. This same property also makes the fibres feel more natural and "sticky" compared to non-polar polymers like polyethylene. In structural applications, Kevlar fibres can be bonded to one another or to other materials to form a composite. Kevlar's main weaknesses are that it decomposes under alkaline conditions or when exposed to chlorine. While it can have a great tensile strength, sometimes in excess of 4.0 GPa, like all fibres it tends to buckle in compression.

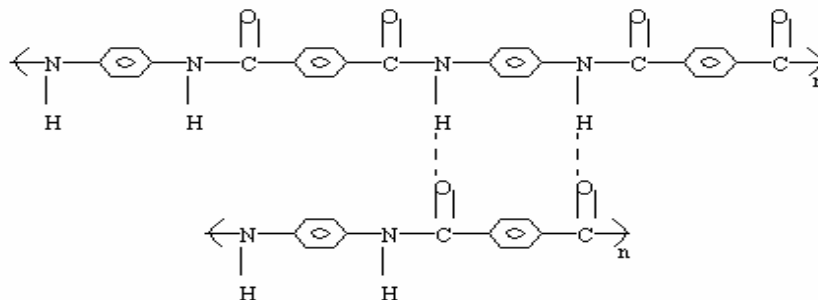


Fig.1.4. Aramid fibre

1.5. Types of Matrix phase used in fibre reinforced polymer composites

Fibres, since they cannot transmit loads from one to another, have limited use in engineering applications. When they are embedded in a matrix material, to form a composite, the matrix serves to bind the fibres together, transfer loads to the fibres, and damage due to handling. The matrix has a strong influence on several mechanical properties of the composite such as transverse modulus and strength, shear properties, and properties in compression. Physical and chemical characteristics of the matrix such as melting or curing temperature, viscosity, and reactivity with fibres influence the choice of fabrication process. The matrix material for a composite system is selected, keeping in view all these factors. Commonly used matrix materials are described below:

1.5.1. Epoxy resin

Epoxy resins are relatively low molecular weight pre-polymers capable of being processed under a variety of conditions. Two important advantages of these resins are over unsaturated polyester resins are: first, they can be partially cured and stored in that state, and second they exhibit low shrinkage during cure. However, the viscosity of conventional epoxy resins is higher and they are more expensive compared to polyester resins. The cured resins have high chemical, corrosion resistance, good mechanical and thermal properties, outstanding adhesion to a variety of substrates, and good electrical properties. Approximately 45% of the total amount of epoxy resins produced is used in protective coatings while the remaining is used in structural applications such as laminates and composites, tooling, moulding, casting, construction, adhesives, etc [3].

Epoxy resins are characterized by the presence of a three-membered ring containing two carbons and an oxygen (epoxy group or epoxide or oxirane ring). Epoxy is the first liquid reaction product of bisphenol-A with excess of epichlorohidrin and this resin is known as diglycidylether of bisphenol A (DGEBA). DGEBA is used extensively in industry due to its high fluidity, processing ease, and good physical properties of the cured of resin.

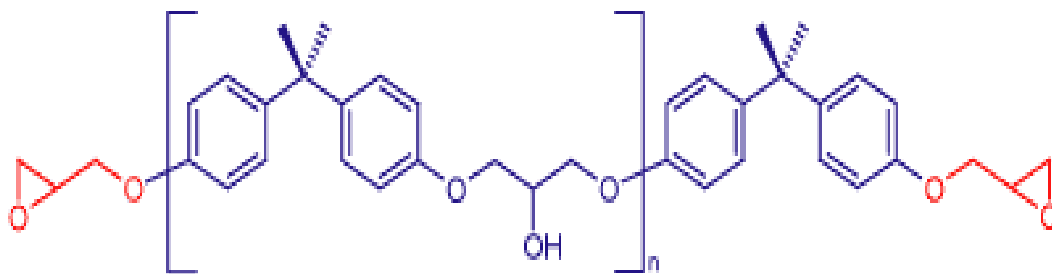


Fig.1.5. Structure of DGEBA

A range of epoxy resins is now available, varying from relatively tough low temperature epoxies for use in construction industry to brittle epoxies for use in construction industry to brittle epoxies useful in aerospace sector. This widespread application of epoxy resin is primarily due to the availability of resins with different backbone structures and molecular weights to give products with low viscosity (liquids) to low melting point solids. The ease of processibility, good melting characteristics, excellent adhesion to various types of substrates, low shrinkage during cure, superior mechanical properties of cured resin, and good thermal and chemical resistance have made epoxy resin a material of choice in advanced fibre reinforced composites.

Ethylene diamines are most widely used aliphatic amines for cured epoxy resins. These are highly reactive, low molecular weight curing agents that result in tightly cross-linked network. One primary amino group reacts with two epoxy groups. The primary and secondary amines are reactive curing agents. The primary amino group is more reactive towards epoxy than secondary amino groups are consumed (95%), whereas only 28% of secondary amino groups are consumed.

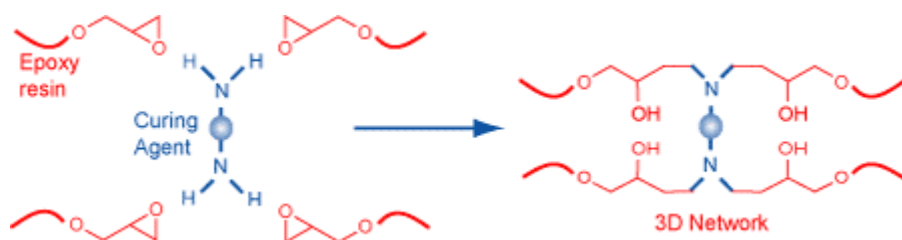


Fig.1.6. The curing of epoxy resin with primary amines

The primary amino-epoxy reaction results in linear polymerization while secondary amino-epoxy reaction leads to branching and cross-linking.

The cured epoxy resins find a variety of applications as adhesives, laminates, sealants, coatings, etc. The optimum curing temperature and the thermal stability of epoxy resin depend

on the type of curing agent. The anhydride cured epoxy resins have excellent electrical, chemical, and mechanical properties and are used for electrical and electronic applications. Epoxies are used as binders in materials for construction. Filling of cracks in concrete structures is achieved by epoxies. In construction industry, for bonding and coating purposes, low temperature curing of epoxies is achieved by using thiols that exhibit higher curing rates. Epoxy based prepregs have been used in numerous aircraft components such as rudders, stabilizers, elevators, wing tips, launching gear doors, radomes, ailerons, etc. The composite materials constitute 3-9% of total structural weight of the commercial aircrafts such as Boeing 767 or Boeing 777. Composite and laminate industry uses 28% of epoxy resins produced. Besides these applications, the applications, the major user of epoxy is coating industry.

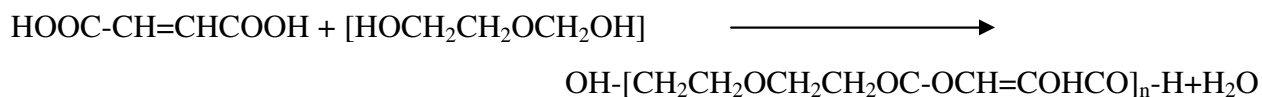
Table 1.6: Typical properties of cast Epoxy Resins (at 23°C)

Property	
Density, g/cm ³	1.2-1.3
Tensile modulus, MPa	55-130
Tensile modulus, GPa	2.75-4.10
Thermal expansion, 10 ⁻⁶ /°C	45-65
Water absorption, %in 24h	0.08-0.15

1.5.2. Unsaturated Polyester Resins

A polyester resin is an unsaturated (reactive) polyester solid dissolved in a polymerizable monomer. Unsaturated polyesters are long-chain linear polymers containing a number of carbon double bonds. They are made by a condensation reaction between a glycol (ethylene, propylene, diethylene glycol) and an unsaturated dibasic acid (maleic or fumaric). The polymerizable (reactive) monomer such as styrene, which also contains carbon double bonds, acts as a cross-linking agent by bridging adjacent polyester molecules at their unsaturated points. The monomer also acts as a diluent, reduces viscosity, and makes it easier to process. The curing or cross-linking process is initiated by adding a small quantity of a catalyst such as organic peroxide or an aliphatic azo compound. Since there is no by-product of the reaction, the curing is done at room

temperature of elevated temperature with or without application of pressure. A typical polyester resin made from reaction of maleic acid and diethylene glycol is shown below:



The length of the molecule or degree of polymerization n may vary. The resin will generally be a solid but is dissolved in a monomer such as styrene. The solution viscosity can be controlled by the percent styrene and is generally quite fluid (less than the viscosity of honey). The conversion from liquid to solid occurs through the use of a free-radical initiator (e.g., benzoyl peroxide) or curing agent. The styrene monomer cross-links or reacts with the double bond in the polyester backbone above to form a network polymer. The reaction does not produce any by-product and is exothermic reaction. Thus, the curing process is accompanied by shrinkage as well as temperature increase.

Capabilities of modifying or tailoring the chemical structure of polyesters by processing techniques and raw materials selection make them versatile [3].

Table1.7: Typical properties of cast Thermosetting Polyesters

Property	
Density, g/cm ³	1.1-1.4
Tensile strength, MPa	34.5-103.5
Tensile modulus, GPa	2-4.4
Thermal expansion, 10 ⁻⁶ /°C	55-100
Water absorption, % in 24h	0.15-0.6

1.6. Applications

The composites industry has begun to recognize that the commercial applications of composites promise to offer much larger business opportunities than the aerospace sector due to the sheer size of transportation industry. Thus the shift of composite applications from aircraft to other commercial uses has become prominent in recent years [7].

Increasingly enabled by the introduction of newer polymer resin matrix materials and high performance reinforcement fibres of glass, carbon and aramid, the penetration of these advanced materials has witnessed a steady expansion in uses and volume. The increased volume has resulted in an expected reduction in costs. High performance FRP can now be found in such diverse applications as composite armouring designed to resist explosive impacts, fuel cylinders for natural gas vehicles, windmill blades, industrial drive shafts, support beams of highway bridges and even paper making rollers. For certain applications, the use of composites rather than metals has in fact resulted in savings of both cost and weight. Some examples are cascades for engines, curved fairing and fillets, replacements for welded metallic parts, cylinders, tubes, ducts, blade containment bands etc.

Further, the need of composite for lighter construction materials and more seismic resistant structures has placed high emphasis on the use of new and advanced materials that not only decreases dead weight but also absorbs the shock & vibration through tailored microstructures. Composites are now extensively being used for rehabilitation/ strengthening of pre-existing structures that have to be retrofitted to make them seismic resistant, or to repair damage caused by seismic activity.

An examination of the diversity of some of these newer applications and the socio-commercial considerations that underpin their introduction gives an instructive insight into the future of high performance FRP.

Unlike conventional materials (e.g., steel), the properties of the composite material can be designed considering the structural aspects. The design of a structural component using composites involves both material and structural design. Composite properties (e.g. stiffness, thermal expansion etc.) can be varied continuously over a broad range of values under the control of the designer. Careful selection of reinforcement type enables finished product characteristics to be tailored to almost any specific engineering requirement.

Whilst the use of composites will be a clear choice in many instances, material selection in others will depend on factors such as working lifetime requirements, number of items to be produced (run length), complexity of product shape, possible savings in assembly costs and on the experience and skills of the designer in tapping the optimum potential of composites. In some instances, best results may be achieved through the use of composites in conjunction with traditional materials.

1.6.1. Composites: The Future Trends

Armed with a wide gamut of advantages, composites have a key role to play in the growing market in India. Composites have made an entry into diverse end-use segments and the developmental efforts for finding newer composites for existing and novel applications is an area of top priority.

1.6.1.1. Transportation Sector

Automobiles

Despite the potential benefits of lighter weight and durability resulting from corrosion resistance, advanced composites is not recognized as a material of choice in the near term for automotive applications. Significant changes on a broad spectrum would be required to make advanced composites attractive for widespread commercial use in cars and trucks. The principal barrier is the high cost of the raw and fabricated materials when compared to existing options.

However there are opportunities for advanced composites in specific components in the commercial automotive sector. In specialty vehicles of several types, produced in small numbers advanced composite materials have an opportunity to demonstrate their performance benefits, apart from the requirements of the competitive marketplace.

The composite industry worldwide is investing in process improvements for the moulding of polymer composites using forms of conventional E-glass in mid-level performance resins, both thermoplastic and thermoset. Automobiles segment of composites accounts for about 50% of the thermoplastic and 24% of the thermoset composite market in the world. Glass-reinforced thermoplastic polymer is a promising material for weight reduction because of the relatively low cost of the fibre, its fast cycle time and its ability to facilitate parts integration. Carbon fibre

reinforced polymer is another candidate but will require breakthroughs in cost and manufacturing techniques to be cost effective for high volume production.

Pressure for reductions in energy use and lower emissions levels makes advanced composites a favourable option for the automotive sector. The composites usage in this sector is estimated around 3500 TPA by 2005 AD. The likely future business opportunities in automotive sector are mentioned below:

- Pultruded Driveshafts
- RTM Panel
- Fiber Glass/Epoxy Springs for Heavy Trucks and Trailers
- Rocker Arm Covers, Suspension Arms, Wheels and Engine Shrouds
- Filament-Wound Fuel Tanks
- Electrical Vehicle Body Components and Assembly Units
- Valve Guides
- Automotive Racing Brakes and Train Brakes
- Clutch Plates

The other area which holds promise for the coming decade is the use of metal matrix composites for certain auto components. The main advantage of such composite material systems is that their physical, mechanical and thermal properties are tailorable and can drastically surpass those of reinforced metals. MMC can be extruded, forged, investment cast, rolled, machined, and heat treated. Transportation applications represent one of the largest demand segments for MMCs, and include turbine and combustion engine components, disc brakes and brake parts, and drive shaft components. Because of their unique properties, metal matrix composites are also gaining interest in a host of high performance applications across a number of industries. Demand for MMCs is growing in the transportation, electronics, telecommunications and pollution control sectors. It is expected that MMCs may experience a double-digit increase across these industrial markets through 2003.

Marine

With composites exhibiting excellent resistance to the marine environment, their applications have made good inroads in the marine sector worldwide. Complex configurations and the

advantages of seamless hulls were the main driving factors in the development of FRP boats. Racing power-boats employ advanced and hybrid composites for a higher performance craft and driver safety. Major structural elements viz. deckhouses, hatch covers, king posts and bow modules appear to be very well suited for FRP construction. In India, composite applications in the marine segment have made some beginning in the last decade in high speed boats, naval vessels, sail boats, fishing boats, high capacity trawlers, barges and other ship components. The consumption of composites by this industry is mainly glass fibre reinforced polyesters.

Advanced composite materials on vessels have a potential to reduce fabrication and maintenance cost, enhance styling, reduce outfit weight and increase reliability. The usage of composites is reckoned at about 750-1000 TPA by 2010 in India. Potential ship applications for composite materials are:

- Shafting Overwraps
- Life rails, Handrails
- Masts, Stacks and Foundations
- Stanchions
- Propellers vanes, Fans and Blowers
- Gear cases
- Valves and Strainers
- Condenser shells

Bicycles

Composite bicycle frames have been a largely American phenomenon, as a spin-off technology from the aircraft and boating industries. Manufacturing of composites requires greater technical expertise and investment for product development. Carbon composite bike frame is a complex structure with performance characteristics that include lightness, rigidity, durability, shock absorption etc. As composites fabrication offers variation over the length of the tube providing different fiber angles, different plies, different ply thickness, different combinations of materials. So the properties of the end product made from composites can be tailored to specifications. Hybrid fibre (carbon and aramid), carbon/kevlar epoxy materials are

ideal composite materials for bicycle components. The composites are finding application in bicycle components such as

- Forks
- Handle bars and Connecting bar ends
- Seat posts

India is yet to make a beginning in utilizing the benefits of composites in bicycle sector. In the near future, India can visualize rapid penetration in the bicycle components market as well as finished cycles. This would however need the back-up of design/ processing technology of a high order, to be able to meet the international standards.

1.6.1.2. Chemical Industry

Supplemented by the advantages of composites of lightweight, mouldability, fire resistance properties, resistance to chemicals has made the material popular in the chemical industry. Composites are extensively used in industrial gratings, structural supports, storage tanks, scrubbers, ducting, piping, exhaust stacks, pumps and blowers, columns, reactors etc. for acidic and alkaline environments.

Some of the potential applications are:

- Composite vessels for liquid natural gas for alternative fuel vehicle
- Racked bottles for fire service, mountain climbing
- Double-wall FRP vessels with an early warning system for leakage detection
- Underground storage tanks
- Casings for electrostatic precipitator
- Drive shafts
- Fan blades (for both axial and centrifugal fans)
- Ducts and Stacks
- Aerial man-lift device

Internationally, composites applications in chemical industry are a relatively small segment in relation to the total usage of composites. However, in India, this forms the major segment

accounting for nearly 28% of total domestic market for composites. With the rapid growth of the chemical industry, this segment is expected to further strengthen with increasing acceptance by the users. The usage of composites in this segment in India is estimated to grow at about 10% p.a. to a level of 11000 TPA by 2005 from the present level of about 5000 TPA.

1.6.1.3. Electrical and Electronics

Composites equipped with good electric insulation, antimagnetic and spark-free, good adhesion to glue and paint, self-extinguishing qualities are used for the construction of distribution pillars, link boxes, profiles for the separation of current-carrying phases to prevent short circuits etc. The other potential applications of composites in this sector are:

- Third rail covers for underground railway
- Structurals for overhead transmission lines for railway
- Power line insulators
- Lightning poles
- Power pole cross arms
- Fibre optic tensile members
- Switchgear frames
- Aerial lift-truck booms

The volume of usage of composites in this segment is projected to increase from the present level of 3000 TPA to about 5000 TPA by 2005 in India.

1.6.1.4. Construction

Construction holds priority for the adaptation of composites in place of conventional materials being used like doors and windows, paneling, furniture, non-structural gratings, long span roof structures, tanks, bridge components and complete bridge systems and other interiors. Components made of composite materials find extensive applications in shuttering supports, special architectural structures imparting aesthetic appearance, large signages etc. with the advantages like corrosion resistance, longer life, low maintenance, ease in workability, fire retardancy etc.

Table1.8. Composite Applications in Building and Construction

Composite	Applications
Coconut/jute/sisal fibre and gypsum plaster	Boards for partitions, ceiling and wall panel
Coconut/jute/sisal fibre and glass fibre with gypsum plaster	Solid and perforated building blocks
Poplar wood with polymer	Door shutters, doors and window frames
Vegetable fibre/red mud and polyester	Flat and corrugated roofing sheets, shutters and tiles
Jute fibre polyester/epoxy with red mud	Panels and sheets, wall cladding, partitions and door shutters
Bagasse and UF/PF resin	Panels and blocks
Coir fibre with fly ash and lime or cement	Bricks and blocks for walling
Glass fibre reinforced polyester	Roofing sheets, partitions, ceilings, sanitary ware, water storage tanks, pipes etc.
Glass fibre reinforced PP/nylon	Door hinges
Red mud plastic (PVC, polyester) reinforced with sisal fibre	Paneling, roofing, partitions, door panels
Acrylic resin and quartz sand composite	Kitchen sinks

Usage of composites for damage repairing, seismic retrofitting and upgrading of concrete bridges finds increased adoption as a way to extend the service life of existing structures, they are also being considered as an economic solution for new bridge structures.

Composite based 2D and 3D grid-type reinforcement for concrete structures shows considerable potential for use as reinforcement of concrete in tunnels because of its corrosion

and chemical resistance, its lightweight and its ease of forming to fit curvatures. Grid-type reinforcement for concrete structures consists of high-performance fibres such as glass, carbon, aramid and hybrids impregnated with resin systems ranging from vinyl esters and other thermosetting resin systems to thermoplastics. The significant systems-level savings were achieved due to the factors of weight.

Other critical applications of composites in the civil engineering area are:

- Tunnel supports
- Supports for storage containers
- Airport facilities such as runways and aprons
- Roads and bridge structures
- Marine and offshore structures
- Concrete slabs
- Power plant facilities
- Architectural features and structures such as exterior walls, handrails, etc.

The worldwide potential for FRP composite repair systems is estimated as at least US \$10 billion per year. The key restricting factors in the application of composites are initial costs due to raw materials and also inefficient moulding processes. With the adoption of advanced technologies and some extent of standardization, these problems could be easily taken care of. A growth rate of 11-13% p.a. in the usage of composites is expected after 2005 AD in this sector.

1.6.1.5. Offshore Oil and Gas Industry

Steel and concrete are the materials of choice for offshore oil and gas production platforms, with steel dominant in the topside applications. Composites have found their way into limited applications, particularly where corrosion and the need to reduce high maintenance costs have been an issue. As the industry moves to greater water depths, the significance of weight saving has become increasingly important in conjunction with the application of buoyant tension for the leg structures. Composites may find excellent usage in fabrication of the following:

- Profiles for oil pollution barriers

- Gratings, ladders and railings on oil-drilling platforms and ships
- Walkway systems
- Sucker rods

1.6.1.6. Consumer and Sports Goods

The optimum design of sports equipment requires the application of a number of disciplines, not only for enhanced performance but also to make the equipment as user-friendly as possible from the standpoint of injury avoidance. In designing sports equipment, the various characteristics of materials must be considered. Among these characteristics are strength, ductility, density, fatigue resistance, toughness, modulus (damping), and cost. To meet the requirements of sports equipment, the materials of choice often consist of a mixture of material types - metals, ceramics, polymers and composite concepts. Following are the general consumer and sports goods where there is lot of potential for composites in the near future:

- Canoes and Kayaks
- Vaulting Pole
- Golf and Polo rods
- Archery equipment
- Javelin
- Hand gliders
- Wind surfer boards

1.7. Objective

The present work includes following projects:

1. Assessment of small interactions and structural gradient at the interface of glass fibre epoxy micro-composites by FTIR-imaging and DSC techniques.
2. Study of cryogenic treatment on the glass/epoxy composites by DSC and flexural (Short Beam Shear) testing techniques.
3. Characterization of small interactions and structural gradient at the interface of glass/ polyester micro-composites by FTIR-imaging and DSC techniques.
4. Finally the SEM micrographs were taken for the hygrothermally and cryogenically treated composite samples.

2. LITERATURE SURVEY

Polymers matrix composites are relevant materials for structural applications such as aerospace, future supersonic, automotive materials because of low density, high specific strength, and high specific modulus [8-9]. They are exposed to environments involving both temperature and humidity. Over the past few years a great deal of experimental work has been done where both physical and mechanical properties of composite materials can be strongly affected during humid ageing and finally affecting the composite performance. In recent years characterization and mechanical behaviour of polymer composites at cryogenic temperature has also been focused. These are the modern engineering materials that have wide applications in a range of areas from aerospace, automobiles and boats to cryogenic equipments such as cryogenic fuel tanks, cryogenic fuel delivery lines, cryogenic wind tunnels and parts of the cryogenic side of turbo-pumps because of their ease of handling, low fabrication cost and excellent mechanical properties. Epoxy resins as the matrix for fibre reinforced plastics have been used in cryogenic tankage in RLV (Reusable Launch Vehicle) thermal insulation, electrical insulation, structural support and adhesives for vacuum tight joints [10], as well as in permeability barriers, which provide minimal structural support in superconducting magnets at low temperatures [11]. When the temperature is decreased down to cryogenic temperature internal stresses are generated in the epoxy matrix due to thermal contraction. Fracture of the matrix is induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the resin. The fracture toughness of the matrix at cryogenic temperature can be improved by controlling the chemical structure, network structure and morphology [12]. The microstructure becomes more orderly at low temperature [13].

2.1. Effect of hygrothermal treatment on glass transition temperature T_g

Glass transition temperature (T_g) of thermoset matrix in composites is very important property because it defines the critical service temperature of the component and consequently their applications. For practical applications they are used at a temperature below their T_g i.e. in the glass state. When materials are exposed to hydrothermal environment, the T_g usually decreases and therefore, the service temperature of the material changes. Moisture absorption by

epoxy matrix composites has plasticizer effect, as reduction of T_g of the matrix. This effect is usually reversible when water is removed but exposure to high temperature can produce irreversible effects, which is attributed to the chemical degradation of the matrix and attack on the fibre/matrix interface. This causes increase of internal voids of the entangling polymer chain, promoting chain expansion and the micro-cracks formation into the polymer matrix [14,15]. There are many factors on which moisture absorption depends such as temperature, fiber volume fraction, reinforcement orientation, fibre nature (i.e. permeability, polarity, and density), and area of exposed surfaces, diffusivity and surface protection.

2.2. Interface and Interphase

The interface/ interphase play a very important role in composite materials. The interface is formed by either chemical or mechanical interaction between fibre and matrix phases [4,7]. Both the fibre and matrix retain their original physical and chemical identities, yet together they produce a combination of mechanical properties that cannot be achieved with either of the constituent acting alone, due to the presence of an interface between these two constituents[16] and interface is in contact and maintains the bond in between for the transfer of load. In contrast interphase is a two dimensional mathematical plane having some finite unknown thickness [17], wherein the chemical, physical and mechanical properties vary either continuously or in a stepwise manner between those of the bulk fibre and the matrix materials[16]. Interphase is a region of chemical inhomogeneity; it is often more susceptible to thermal or chemical degradation than either bulk phase. For this reason, the interphase may provide an easy path into the composite for aggressive agents, notably water. The interphase region is up to few nanometers and the short range forces exist between the monomer segments and the solid surface. These interactions may range from weak dispersion (Van der Waals) forces to chemical attachments [17].

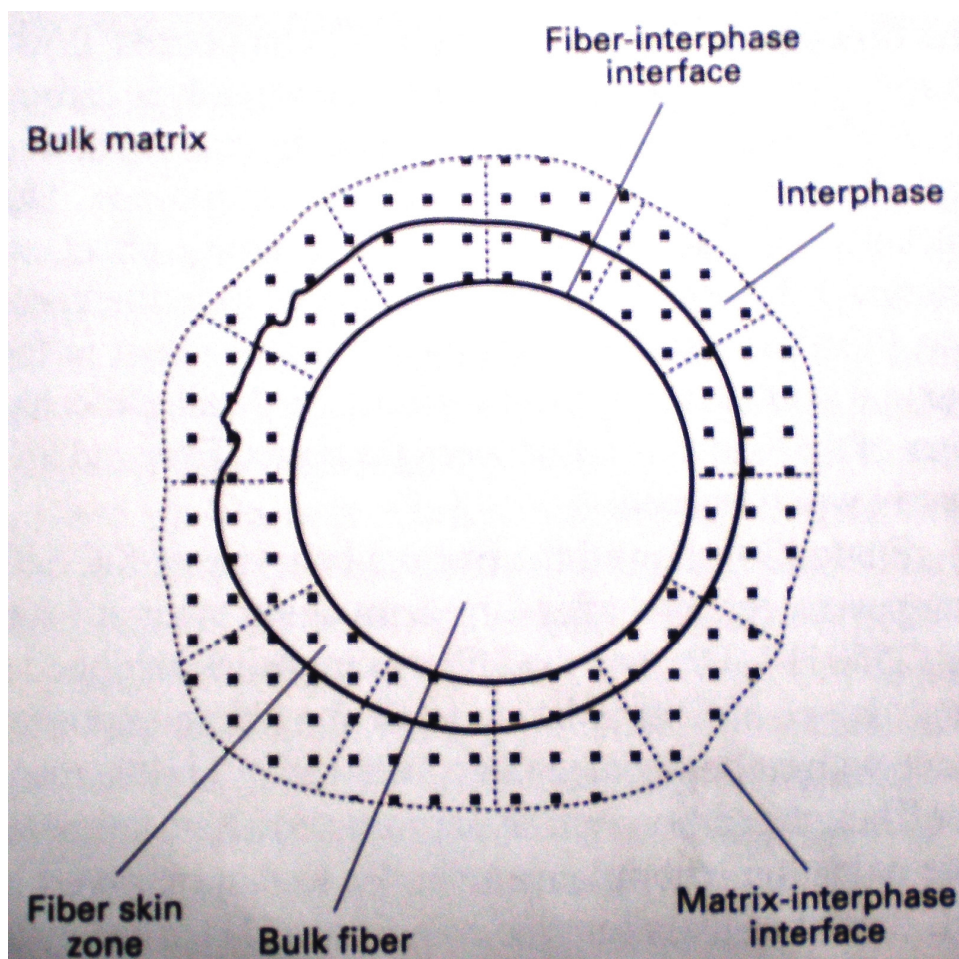
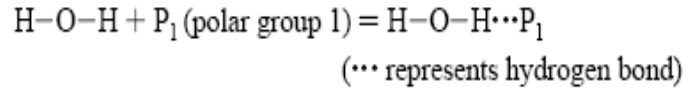


Fig.2.1. Interface and interphase

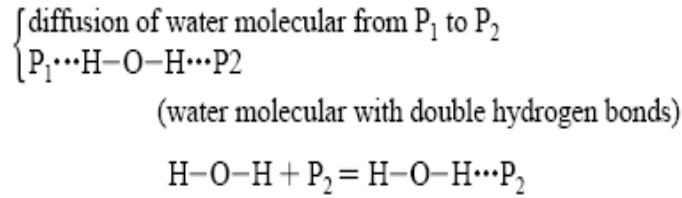
2.3. Dual nature of water sorption in epoxy resin

Epoxy resins are commonly used as adhesives, coatings and in composites materials. They have good combination of chemical, thermal, electrical and mechanical properties but in many applications they have the disadvantage of absorption of water because of the large amount of polar OH groups in the structure which is susceptible to the polar water molecules. Absorption of water in epoxy resins leads to plasticization, the hydrolysis reactions (scission of polymer chains) and this causes decrease in the glass transition temperature T_g (it is reported that for every 1% absorption of moisture there is decrease of 20°C), swelling stresses may be generated.[3]. Diffusion of water was studied in many epoxy resin in which in addition of plasticization double bonds has also been seen in which double bond acting as a physical cross-link which causes increase of T_g in epoxy resins. But it is not evident that after how long period

of sorption water molecule can form double hydrogen bonds. On the contrary it has been found that in the initial stage of sorption experiments, water molecules with double hydrogen bonds were generally observed in different epoxy systems [18]. The water sorption at the interface shows a dual nature. The water may be present as free molecule or in combined form by forming double hydrogen bond with the hydrophilic group of epoxy resins. The formation of double hydrogen bond is clear from the following diagram:



Open a new polar group P_2 (polar group 2)



A second system that has been studied extensively because of its technical importance is the adhesion between epoxy resins and glass, particularly glass fibres. To improve the hydrolytic stability of the composite, the glass surfaces are normally modified by covering them with a thin layer of a silane adhesion promoter. These silanes are well known to self-assemble into mono-molecular and multi-molecular layers on surfaces such as glass or silicon dioxide. One end of the silane molecule typically has di or tri methoxy or ethoxy functionality whilst the other end normally has amine or epoxy functionality. The ethoxy functionality is believed to condense with the hydroxyl functionality on the surface of the glass whilst the amine functionality can react with the epoxy, as shown in Fig2.2. Hence it is attractive to suggest a simple picture of a single molecular layer of silane adhesion promoter between the epoxy and the glass. However the real situation is much more complex. The amount of silane typically used is much too great to form a monolayer. Also as the silane has multi methoxy or ethoxy functionality it can self condense. The relatively thick layer of silane is believed to form a network and then the epoxy both mixes into and reacts with the network. Although it is clear that the silane causes covalent bonding between the glass and the epoxy, there is no way to estimate the actual density of coupling produced. It is interesting to note that fairly good adhesion can be obtained in dry conditions without the silane, however it has a profound effect on adhesion in the presence of water.

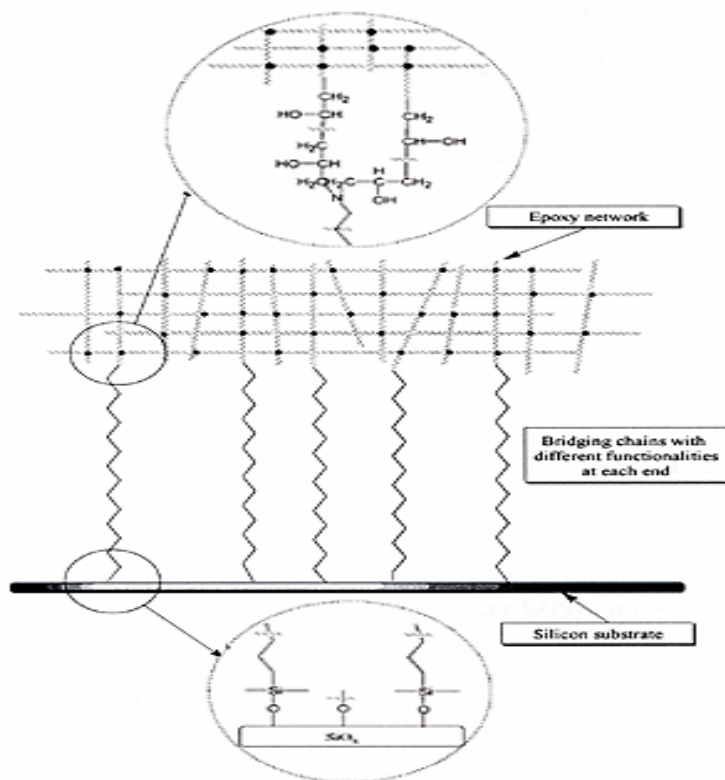


Fig.2.2. The way bridging chains, with silane functionality at one end and amine functionality at the other, can form covalent links between an epoxy network and glass substrate.

Moisture absorption is a matrix dominating property in fibre reinforced polymer composites. The fibre plays a role as much as the interface region between the fibre and the matrix may be of deferent network structure to that of the bulk matrix away from the fibre. This leads to the composite absorbing different amount of penetrant (i.e. water) per unit mass of resin than the bulk polymer [19]. The process of moisture absorption into the GRFP and CRFP is often considered to be driven by simple Fickian diffusion.

2.4. Formation of hydrogen bond at the interface of FRP composites due to hygrothermal diffusion

The water must have penetrated through the fibre/matrix interphase. Previous studies have shown that water at the interphase causes replacement of the covalent bonds, between the siloxane backbone of the sizing material and the glass surface, with hydrogen bonds between the

chemical moieties on the fibre glass surface (moieties containing oxygen atoms), water molecules at the interphase, and the hydroxyl groups on the sizing material.

The presence of water at the interphase causes the covalent chemical bonds between the silane coupling agent and the glass surface to transform into strong physical interactions via formation of hydrogen bonds between the glass surface, water molecules and the network of silane coupling agents. Previous works on formation of silane network on glass fibres have shown that the siloxane network does not cover the glass fibre continuously as a monolayer film. It rather forms islands of three-dimensional network on glass fibre. This is demonstrated schematically in Fig.2.3.(a). where the fibre is shown to be bonded to the matrix at certain spots. The presence of water in the matrix and at the interface in conjunction with the axial load may increase the effective contact area/region between fibre and matrix, in which strong physical interactions can create adhesion between fibre and matrix. This is shown in Fig.2.3.(b). In this figure, it is shown that although the chemical bonds between fibre and matrix are broken, the presence of water has created a region where larger surfaces of fibre and matrix (compared to the unconditioned case) participate in the adhesion process. This larger contact area/region allows the load to transfer to the fibre more effectively thus maintaining the strength [20].

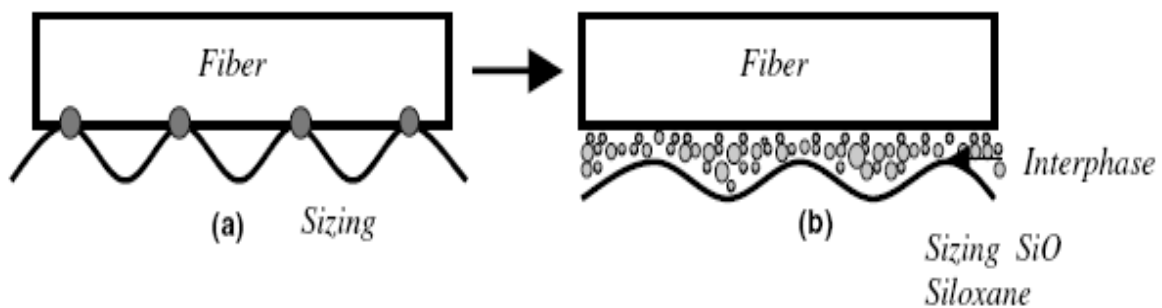


Fig.2.3. (a) Control specimens, (b) Conditioned specimens with hydrogen bonds forming at elevated temperatures.

2.5. Hygrothermal diffusion processess

Hygrothermal Diffusion usually takes place in presence of thermal and moisture gradients.

Types of Hygrothermal diffusion

2.5.1. Fickian and Non-Fickian Diffusion

In many cases water absorption obeys Fick's Law and diffusion is driven by the moisture concentration gradient between the environment and material producing continuous absorption until saturation is reached. The atoms migrate from region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise in temperature. The concentration gradient of moisture is developed due to the non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion. Epoxy resin absorbs water from the atmosphere from the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of water into all the material. The water absorbed is not usually in liquid form but consists of molecules or group of molecules linked by hydrogen bonds to the polymer. In addition water can be absorbed by capillary action along any crack which may be present or along the fibre-matrix interface.

The Fickian diffusion process is influenced mainly by two factors:

1. The internal (fibre volume fraction and its orientation)
2. The external (relative humidity and temperature).

Stage 1: Moisture absorption is Fickian.

Stage 2: There is a deviation from linearity with the time axis (reaching saturation, so decrease in slope).

Stage 3: Non- Fickian pattern (there is a development of micro cracks which enable rapid moisture diffusion, so rapid increase in percentage of moisture).

Non- Fickian behavior

Fickian behaviour is observed in the rubbery state of polymers but often fails to diffusion behaviour in glassy polymers. The deviation from Fickian behavior occurs when:-

- a) Cracks or delamination develops.
- b) Moisture diffusion takes place along the fibre matrix interface.
- c) Presence of voids in the matrix.

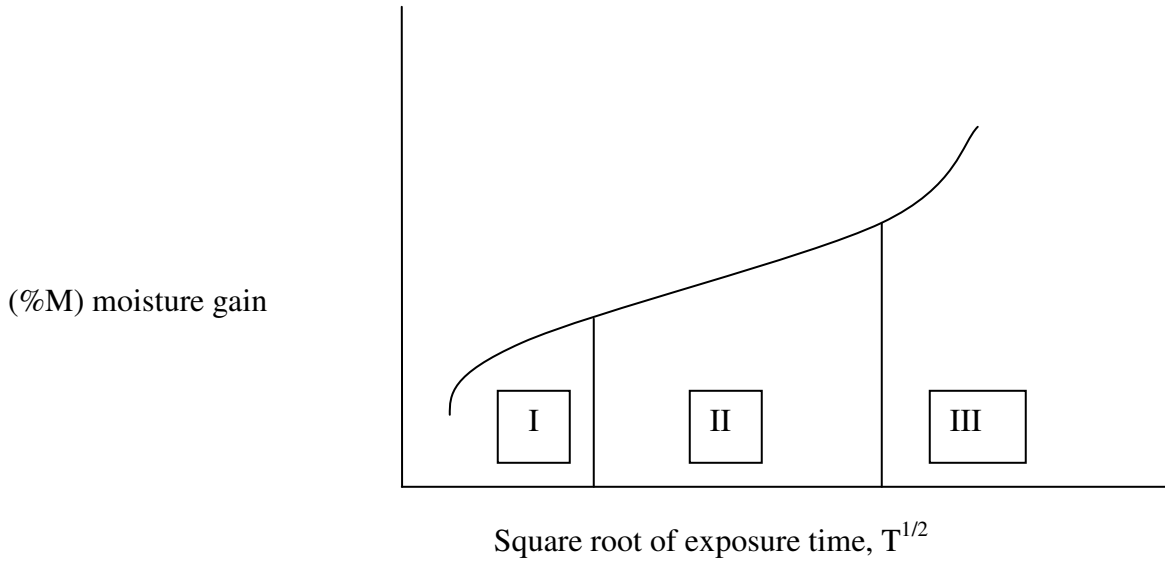


Fig.2.4. Description of the different stages in moisture absorption kinetics

The nature of diffusion behavior whether Fickian or non Fickian depends on the relative rate at which the polymer structure and the moisture distributions change. When the diffusion rates are much slower than the rate of relaxation, the diffusion has to be Fickian. Non Fickian behavior pertains to the situations when the relaxation processes progress at a rate comparable to the diffusion process. Hydrothermal diffusion in polymeric composites is mostly Fickian type, but non-Fickian behavior is also common for glass/epoxy composite. Absorbed moisture in the composite certainly deteriorates the matrix dominated properties but this effect is more pronounced at higher temperatures and at lower strain rates. The ILSS values are the worst affected property due to this moisture absorption [21].

In simple Fickian diffusion is a process in which transport of the water is a diffusion process driven by the water concentration gradient. However in epoxy reinforced glass and carbon composites there is mismatch between the amounts of moisture absorbed by the matrix resin is significantly different than that of the reinforcement fibre.

2.5.2. Langmuir Diffusion

Diffusion of water within the polymer and its kinetics are clearly intrinsically related to the degradation process. The classic Fickian treatment has often been used to explain water

uptake by epoxy resins but this is not always adequate. In a classic paper by Carter and Kibler, dating back to 1978, the so-called Langmuir-type (by virtue of its similarity to Langmuir adsorption) diffusion model was developed. When mass increase is represented as a function of the square root of ageing time, the initial linear portion of the curve, successfully described by the Fick (constant diffusion coefficient) treatment, transforms at later times to an essentially linear part of lower, but non-zero, gradient (thus precluding evaluation of a diffusion coefficient due to the lack of an asymptotic saturation value of water uptake). Carter and Kibler suggested a model involving bound water and mobile (free) water, with γ (respectively β) the probability per unit time (in s^{-1}) for free (respectively bound) molecules to become bound (respectively free). Considering $n(t)$ mobile water molecules and $N(t)$ bound molecules per unit volume at time t , at equilibrium (suffix N) we have

$$\gamma n_{\infty} = \beta N_{\infty} \quad (1)$$

The model has been used with some success at times. Several studies have been effected to clarify the existence, and form, of the bound and free water components in epoxies, as partially reviewed by Feng et al., who themselves used infrared spectroscopy as their main experimental technique in an attempt to differentiate between the two ‘types’. Various propositions have been made concerning this dual-sorption invoking, for example, voids within the polymer, hydrogen bonding and heterogeneous morphology. However, the literature often shows simplistic or, at the other extreme, complex interpretations, sometimes with limited agreement between experimental data and models. Another problem is that ageing is often over relatively short periods and in humid atmospheres, rather than by immersion, leaving some doubt as to final equilibrium [22].

2.5.2.1. Basis of Carter and Kibler model

Carter and Kibler assume that the diffusion of mobile molecules conforms to simple diffusion theory, modified by sources and sinks. For the one-dimensional case, the molecular number densities at position z and time t satisfy the coupled pair of equations

$$D \frac{\partial^2 n}{\partial z^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \quad (2)$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \quad (3)$$

where D is a (constant) coefficient of diffusion. The n represents the number of mobile molecules (per unit volume) with a probability γ (s^{-1}) to become bound and N the number of bound molecules with a probability β (s^{-1}) to become mobile. In the experimental case, for a sample thickness $e=2\delta$, $z=0$ representing the central plane with surfaces at $z=\pm \delta$, exposed to a constant moisture environment on both sides at $t=0$, the boundary and initial conditions are

$$n(z, 0) = 0 \text{ and } N(z, 0) = 0 \text{ for } |z| < \delta$$

and

$$n(\delta, t) = n_\infty \text{ and } n(-\delta, t) = n_\infty \text{ for all } t$$

At a given thickness z and time t , the number of n -type molecules is

$$\begin{aligned} n(z, t) = n_\infty & \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)(r_{2n+1}^+ - r_{2n+1}^-)} \right. \\ & \times \left[r_{2n+1}^+ e^{-r_{2n+1}^- t} - r_{2n+1}^- e^{-r_{2n+1}^+ t} \right] \cos\left(\frac{\pi(2n+1)z}{2\delta}\right) \Big\} \\ & + n_\infty \frac{4}{\pi\beta} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)(r_{2n+1}^+ - r_{2n+1}^-)} \\ & \times (r_{2n+1}^+ r_{2n+1}^-) \left[e^{-r_{2n+1}^- t} - e^{-r_{2n+1}^+ t} \right] \cos\left(\frac{\pi(2n+1)z}{2\delta}\right) \end{aligned} \quad (4)$$

where

$$\begin{aligned} r_{2n+1}^\pm &= \frac{1}{2}(\kappa(2n+1)^2 + \gamma + \beta) \\ & \pm \sqrt{(\kappa(2n+1)^2 + \gamma + \beta)^2 - 4\kappa\beta(2n+1)^2} \end{aligned} \quad (5)$$

and

$$\kappa = \frac{\pi^2 D}{(2\delta)^2} \quad (6)$$

In many applications of the Carter and Kibler theory to present water diffusion in polymers, it has been common to be contented with overall water uptake as a datum. In the following, we wish to consider separately the mobile and bound contributions, respectively $n(z,t)$ and $N(z,t)$. To do this, it is convenient to rearrange Eq. (3) and solve it by use of an integrating factor, $e^{+\beta t}$, leading to

$$N(z,t) = \gamma e^{-\beta t} \int n(z,t) e^{\beta t} dt \quad (7)$$

Let N be the total number of water molecules per unit area perpendicular to z in the polymer at saturation ($+\delta > z > -\delta$). The equilibrium is defined by

$$2\delta(n_\infty + N_\infty) = N \quad (8)$$

Use of Eqs. (1) and (6) leads to

$$n_\infty = \frac{\beta}{\gamma + \beta} \frac{N}{2\delta} \quad (9)$$

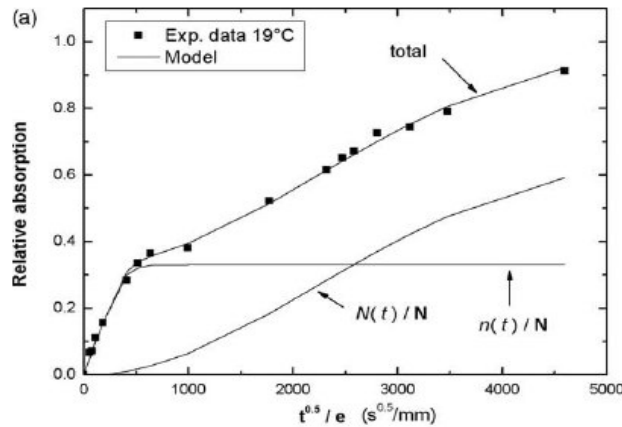
With judicious approximation, we obtain, for the case β and $\gamma \ll \kappa$

$$\frac{n(t)}{N} = \frac{\beta}{\gamma + \beta} \left\{ 1 - \frac{8}{\pi^2} e^{-\kappa t} \right\} \quad (10)$$

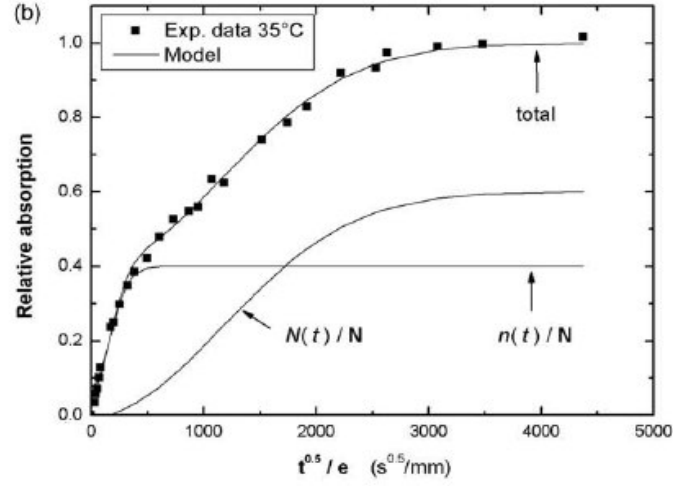
$$\frac{N(t)}{N} = \frac{\gamma\beta}{\gamma + \beta} e^{-\beta t} \left\{ \frac{1}{\beta} (e^{\beta t} - 1) - \frac{8}{\pi^2 \kappa} (e^{-\kappa t} - 1) \right\} \quad (11)$$

Useful approximations are given below, with $N(t) = n(t) + N(t)$ the total amount of water molecules in polymer at time t . For short exposure time

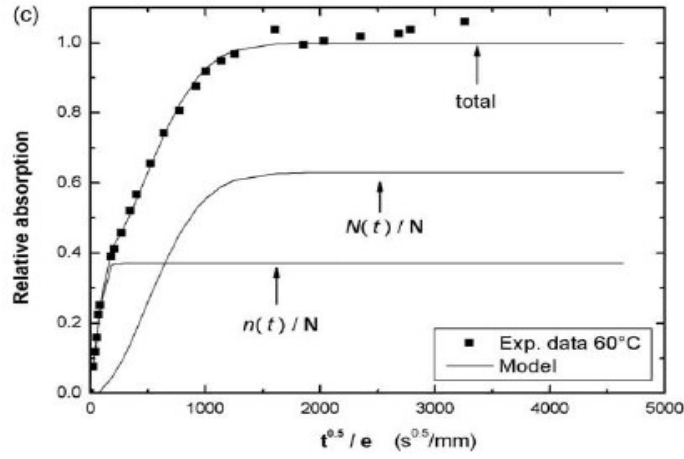
$$\frac{N(t)}{N} \cong \frac{4}{\pi^{3/2}} \left(\frac{\beta}{\beta + \gamma} \right) \sqrt{\kappa t} \quad (12)$$



(a)



(b)



(c)

Fig.2.5. Gravimetric data for water absorption in de-ionised water at (a) 19°C, (b) 35°C, (c) 60°C. (■) experimental, (—) model.

For long exposure time

$$\frac{N(t)}{N} \cong \left(1 - \frac{\gamma}{\beta + \gamma} e^{-\beta t}\right) \quad (13)$$

The ratio $N(t)/N$ seems to be consistent with a pseudoequilibrium moisture content which appears at medium times.

The value of the pseudo-equilibrium is

$$\frac{N(t_{\text{pseudo-eq.}})}{N} = \frac{\beta}{\beta + \gamma} \quad (14)$$

Hence the this result in a significant mismatch in moisture induced volumetric expansion between fibres, and thus leads to localizes stresses and strain fields in fibrous composites [19]. Water may be present in the composite either at preferential sites such as interface and may be in the free molecules or clustered group. This shows the dual sorption. Another important mechanism is hygroelastic swelling of the polymer as the constituent macromolecules rearrange to relieve the osmotic pressure generated by the water molecules. It has been observed that absorption of moisture causes degradation of matrix- dominating properties such as interlaminar shear strength and in $-$ plane shear strength, and compressive modulus and strength [3]. The longitudinal strength has actually been shown to increase slightly with initial absorption and this may reflect for instance reduced flaw sensitivity in the matrix as a result of plasticization or improved ability to transfer stress efficiently in the region of a fiber break. All properties are appear to be reversible, at least to a large extent, on drying out, provided that there is no moisture induced permanent damage, e.g. in the form of micro cracking [15].

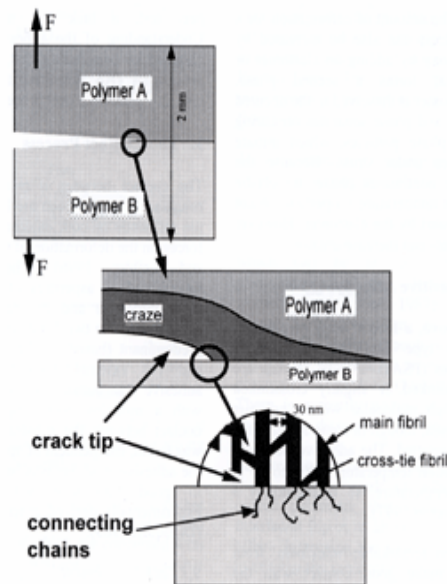


Fig.2.6. The structures at the crack tip in a crazing material.

It was also proved that in the initial stages of thermal and cryogenic conditioning shear strength improves and high temperature conditioning contributes more strengthening effect and better adhesion at the interface [19].

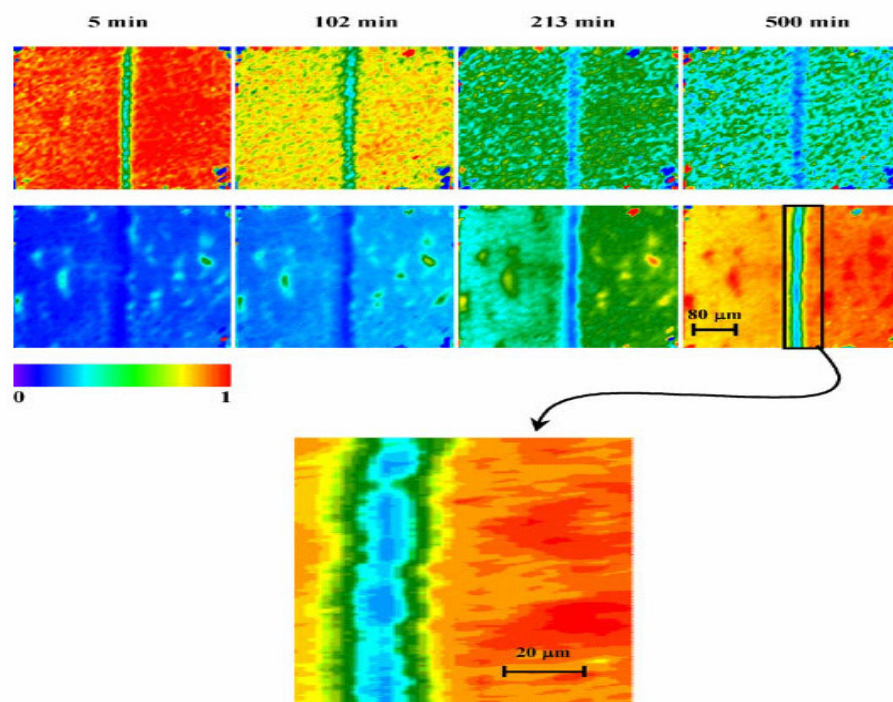


Fig.2.7. Chemically specific images (IR absorption) of the amine groups, H–N–H (top), and hydroxyl groups, OH (middle), as a function of the curing time. The bar range from 1 to 0, indicating a relative absorbance scale.

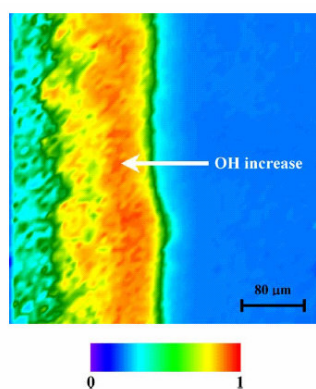


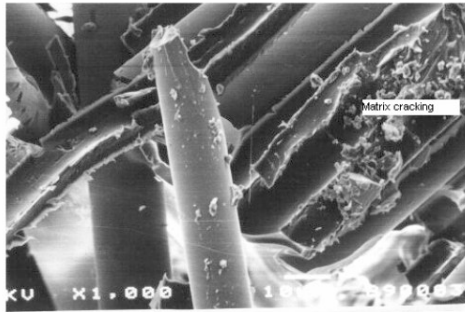
Fig.2.8. Image corresponding to the OH signal for the poly (aminopropylsiloxane) sample. The bar ranging from 1 to 0 indicates a relative absorbance scale.

High temperature ageing not only increases the moisture uptake rate but it may modify the local stress that is required for delamination nucleation [23].

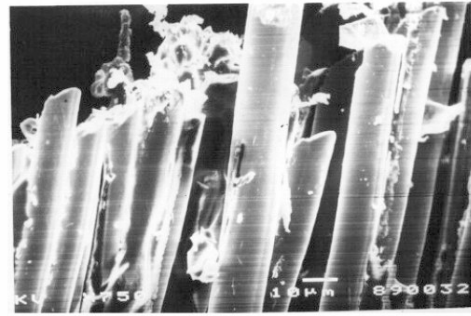
To obtain a clear picture of diffusion process, various techniques have been employed in this field, such as near-infrared Fourier transform infrared spectroscopy (NIR-FTIR), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), ultraviolet (UV) reflection, solid state nuclear magnetic resonance (NMR), dielectric relaxation measurements,

positron annihilation lifetime spectroscopy (PALS), electrochemical impedance spectroscopy (EIS), fluorescence and molecular simulations. In this case FTIR imaging in mid-infra red range is used.

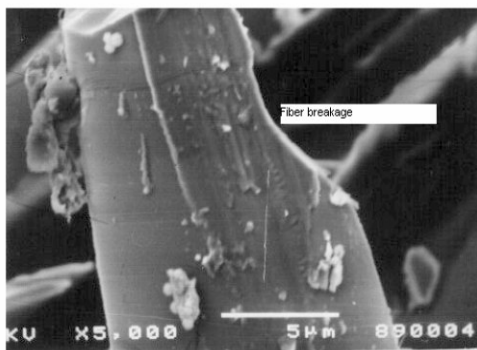
2.6. Various failure modes of FRP composites due to humid ageing



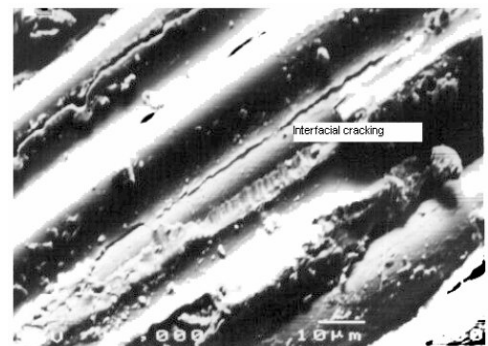
2.9.(a)



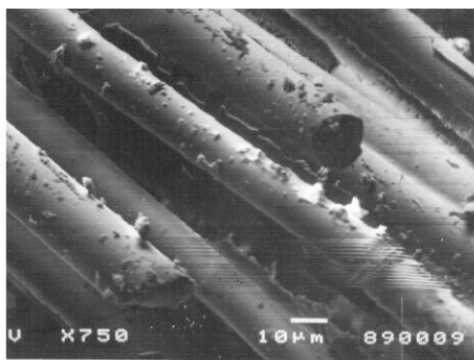
2.9.(b)



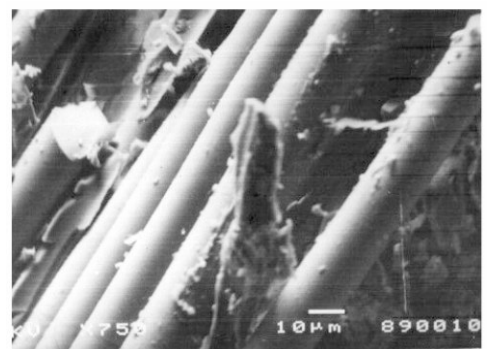
2.9.(c)



2.9.(d)



2.9.(e)



2.9.(f)

Fig.2.9. (a)-2.9.(c) Scanning electron micrograph shows matrix cracking and fibre damage in carbon/epoxy composites [19].

Fig.2.9. (d)-2.9.(f) De-adherence and interfacial cracking is evident in aged glass/epoxy laminated composites [19].

2.7. Effect of Cryogenic Treatment on the of FRP composites

Structural polymer matrix composites were rarely exposed to hundreds of thermal cycles from extremely low temperature to an elevated maximum service temperature. Last 20 years ago these composites were considered for satellite applications where dimensional stability is considered to be very important. In this case the variation of temperature is in a range of +125 to -155 °C when orbiting the earth. Cryogenic liquid fuel is preferred to solid fuel of propellants of launch vehicles and rockets in aerospace applications because of their high specific impulse; the low calorific energy to volume ratio of the cryogenic liquid fuels makes the pressurized tanks large and heavy when made up of metallic materials. So now PMCs are contenders for use in reusable launch vehicle components. Mostly such components are cryogenic fuel tanks, cryogenic fuel delivery lines, and parts of the cryogenic side of turbo-pumps [24] which are made up of carbon/polymer composites [25]. Polymer matrix composite are good candidates to design components of primary structures of the future supersonic aircrafts. In this case also the components are also exposed to very harsh environment as the structures are subjected to temperature variation in the range of -55°C(subsonic flight) and +130°C(super sonic flight)[26]. These are increasingly being used in civil infrastructure in application ranging from reinforcing rods and tendons, wraps for seismic retrofit of columns and externally bonded reinforcement for strengthening of walls, beams, and slabs, to all-composite bridge decks, and even hybrid FRP composite in combination with conventional materials for structural systems [27]. Today fibre reinforced polymer composites has become one of the most important branches of modern engineering with wide range of application from aircraft and boats to cryogenic equipments. Glass reinforced polymer composites are used mainly in thermal insulation, electrical insulation, and structural support, as well as in permeability barriers, which provide minimal structural support in superconducting magnets at low temperatures [28].

At high temperatures there is always sufficient thermal energy available to the molecules to allow easy rotation, movement and disentanglement. But at low temperatures there is little energy available and molecular motion is inhibited. So whenever there is a thermal reversal there is change in properties. Many works have been carried out to understand the dramatic changes that occur in the structure and properties of the composite material when they are exposed to cryogenic temperatures [29].

The behaviour of a composite to change in temperature is for two main reasons. Firstly the matrix response to an applied load is temperature dependent and secondly, change in temperature can cause internal stresses to be set up as a result of differential thermal contraction and expansion of the two constituents [7]. These stresses affect the thermal expansivity i.e. the expansion coefficient of the composite. Potholing or localized surface degradation, delamination, and micro cracking are some of the more dramatic phenomena that can occur as a result of cryogenic cycling [30].

Increased thermal stresses are the underlying cause of micro cracking in composites at cryogenic temperatures. As the laminate temperature falls below its stress-free temperature, residual stresses develop in the material. These stresses are the result of a difference in the linear coefficient of thermal expansion (CTE) between the fibers and the matrix [29,31,32].

The generated residual stresses influence the overall thermo-mechanical properties of the composite. In some cases, the resulting stresses are sufficient to initiate plastic deformation within the matrix immediately around the fibre. Therefore, it is important to determine the current state of the residual stresses and their effects on the behavior of the composite when subsequently subjected to various uniaxial and multiaxial mechanical loading [33,34]. The stresses can also be large enough to initiate material damage such as matrix micro cracking. These micro cracks can reduce both the stiffness and the strength of the material, as well as act as sites for environmental degradation and nucleation of macro cracks [35].

3. METHODS AND MATERIALS

3.1 METHODS

3.1.1 Fourier Transform Infrared (FTIR) Spectroscopy

3.1.1.1. Principle

Infrared spectroscopy is a widely used technique that for many years from 4000cm^{-1} to 667cm^{-1} and results from vibrational plus rotational transitions. This region is particularly meant for organic chemists since the vibrations induced in organic molecules are absorbed in this region.

The regions on either side of the infrared are known as near infrared (12500cm^{-1} to 4000cm^{-1}) and far infrared (667cm^{-1} to 50cm^{-1}) regions. The near infrared region exhibits bands assignable to harmonic overtones of fundamental bands and combination bands whereas the far infrared region deals with the pure rotational motion of the molecules. The normal infrared region (also called middle infrared region) extends. The combination of infrared spectroscopy with the theories of reflection has made advances in surface analysis possible. Specific IR reflectance techniques may be divided into the areas of specular reflectance, diffuse reflectance, and internal reflectance. In our case internal reflectance is used. This is a technique for monitoring the transport process of low molecular weight species was established based upon these concepts. This enabled the monitoring of individual species in-situ, while providing additional chemical information on any changes that may be occurring during the transport process. The in-situ evaluation of diffusivity is dependent upon the ability to quantify the FTIR-ATR spectra obtained. The IR absorbance values of a sample are related to its concentration, analogous to the way concentration is related to absorbance in transmission spectroscopy through the Beer-Lambert law.

Only those vibrations that result in the change of molecular dipole (separation of positive and negative charges) and having absorption frequencies in the infrared region of the spectrum

absorb infrared radiation. Simple gas molecules such as H_2 , Cl_2 and O_2 do not have dipoles and therefore do not give infrared spectra. However, molecules such as SO_2 and CO_2 do have dipoles, hence they have infrared spectra.

The physical property that is measured in infrared spectroscopy is the ability of some molecules to absorb infrared radiation. Atoms in molecules are not static, as one might think, but rather they vibrate about their equilibrium positions. The frequency of these vibrations depends on the mass of the atom and the length and strength of the bonds. Molecular vibrations are stimulated by bonds absorbing radiation of the same frequency as their natural vibrational frequency (usually in the infrared region). For each molecule a variety of vibrations is possible, such as:

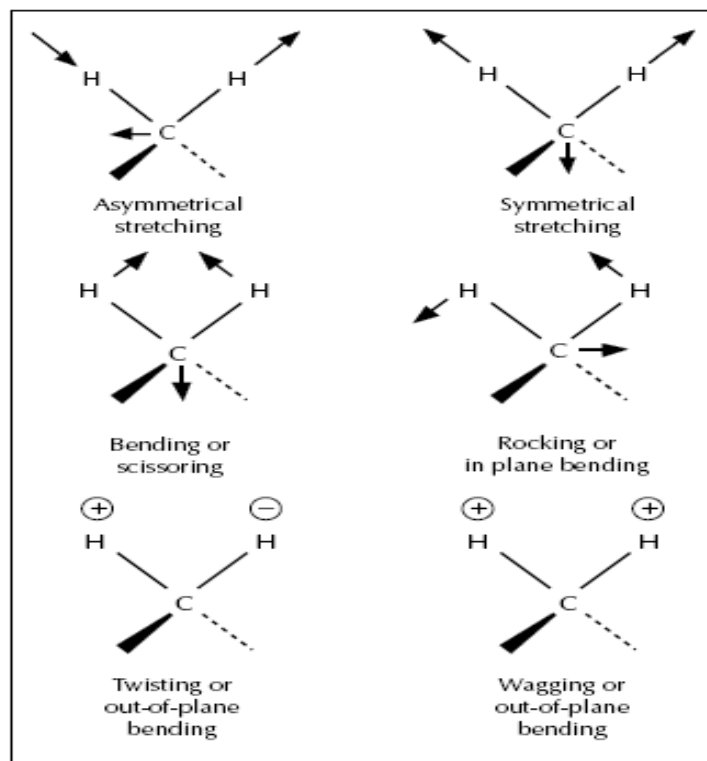


Fig.3.1. Types of vibrations: the + and – symbols indicate a movement out of and into the plane of the paper respectively

Fourier Transform Infrared Spectroscopy (FTIR) works by exciting chemical bonds with infrared light and is best for identification of organic materials. The different chemical bonds in this excited state absorb the light energy at frequencies unique to the various bonds. This activity is represented as a spectrum (Fig.3.2.)

The spectrum can be expressed as % transmittance (%T) or % absorbance (%A) versus wavenumber. The wavenumber of the peak tells what types of bonds are present and the %T tells the signal strength. Low signal strength directly affects the resolution of the peaks making sample size and preparation key for acquiring a quality spectrum [36-37].

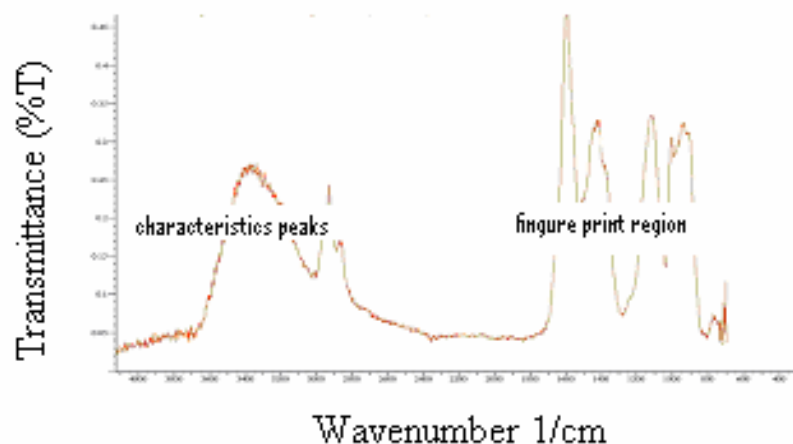


Fig.3.2. FTIR spectra

The region of the infrared spectrum from 4000cm^{-1} - 1400cm^{-1} exhibit absorption bands falls under the functional group regions. These bands are useful diagnostically but more usually they supplement the region below 1400cm^{-1} .

The region from 1400cm^{-1} to 900cm^{-1} is complex because it contains apart from fundamental stretching and bending vibrations many bands resulting from the sum or difference of their vibration frequencies. Specific vibrational assignments in this region are, therefore, very difficult. Thus, this part of the spectrum is characteristic of a compound and is called finger-print region. Similar molecules may show very similar spectra in the functional group region but certainly exhibit discernible differences in the finger-print region.

A ratio of specific peak heights can sometimes be used to quantify proportions in simple mixtures, degree of oxidation or decomposition, purity, etc. The FTIR aids in identifying chemical bonds, and thus chemical composition of materials. FTIR imaging suggests that there is a chemical gradient near the interface of the composite materials [23]. Fourier transform infrared spectroscopy is a technique for obtaining high quality infrared spectra by some mathematical conversion of an interference pattern into a spectrum. The FTIR spectrometer includes Michelson interferometer and is shown (Fig.3.3.):

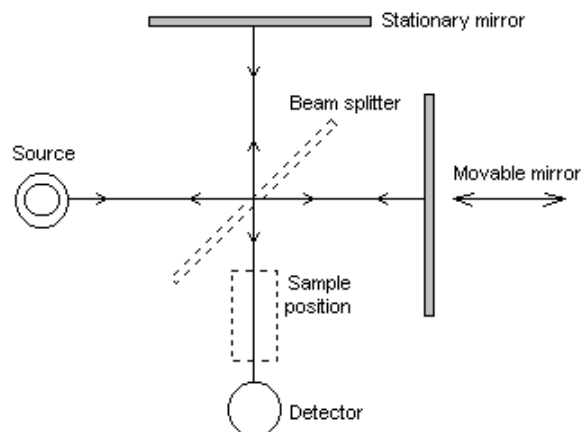


Fig.3.3. Michelson interferometer set-up

Radiation leaves the source and is split. Half is reflected to a stationary mirror and then back to the splitter. This radiation has travelled a fixed distance. The other half of the radiation from the source passes through the splitter and is reflected back by a movable mirror. Therefore, the path length of this beam is variable. The two reflected beams recombine at the splitter, and they interfere (e.g. for any one wavelength, interference will be constructive if the difference in path lengths is an exact multiple of the wavelength. If the difference in path lengths is half the wavelength then destructive interference will result). If the movable mirror moves away from the beam splitter at a constant speed, radiation reaching the detector goes through a steady sequence of maxima and minima as the interference alternates between constructive and destructive phases. In the FTIR instrument, the sample is placed between the output of the interferometer and the detector. The sample absorbs radiation of particular wavelengths. Therefore, the interferogram contains the spectrum of the source minus the spectrum of the sample. An interferogram of a reference (sample cell and solvent) is needed to obtain the spectrum of the sample.

After an interferogram has been collected, a computer performs a Fast Fourier Transform, which results in a frequency domain trace (i.e. intensity vs. wavenumber) that we all know and love. The detector used in an FT-IR instrument must respond quickly because intensity changes are rapid (the moving mirror moves quickly). Thermal detectors are too slow so liquid nitrogen cooled mercury-cadmium telluride detector is used for extreme sensitivity. To achieve a good signal to noise ratio, many interferograms are obtained and then averaged. This can be done in less time than it would take a dispersive instrument to record one scan.

Fourier Transform Infrared (FTIR) spectroscopy is said to be the most versatile, fast, inexpensive, and conclusive method for surface and bulk characterization. As a result, FTIR spectrometers are found in most laboratories. The main component of the FTIR spectrometer is the Michelson interferometer, invented in 1880 by Albert Abraham Michelson, who was awarded the Nobel Prize in Physics in 1907. The major advantage of a FTIR spectrometer over a dispersive infrared spectrometer is that the signal-to-noise ratio (SNR) is quite high. SNR is defined as the ratio of the amplitude of a spectral band at any point to the amplitude of the noise at some baseline point nearby in the spectrum. Noise is observed when there are some fluctuations in the spectrum above and below the baseline.

FTIR spectroscopy has been classified into two major areas: non-reflection techniques and reflection techniques. Table3.1. distinguishes different techniques within both areas while Table3.2. gives some information about their penetration depth range and surface requirements.

Table3.1. Non-reflection and reflection techniques

Non-reflection techniques: Emission spectroscopy (EMS) Photothermal beam deflection spectroscopy (PBDS) Photoacoustic spectroscopy (PAS) Transmission spectroscopy
Reflection techniques: External spectroscopy (ERS) Reflection-absorption spectroscopy (RAS) Grazing incidence reflection (GIR) Internal spectroscopy (IRS) Multiple internal reflection (MIR) Frustrated total reflection (FTR) Attenuated total reflectance (ATR) Diffuse reflectance (DRIFT)

Table3.2. Penetration depth and surface requirements for some FTIR surface techniques.

Technique	Penetration depth range	Surface
RAS	submonolayer to 2 μm	coated metallic
PAS, PBDS	200 Å to 50 μm	any shape
EMS	100 Å to 5 μm	any surface
DRIFT	monolayer to few μm	powder, fiber
ATR	40 Å to 3 μm	smooth film

Attenuated Total Reflectance (ATR) spectroscopy has been used to measure interdiffusion for a number of polymer systems. This technique is attractive for several reasons. It is easy, simple and nondestructive, and the penetration depth ranges between 0.1 to 10 mm. Any concentration change within the penetration depth due to diffusion of one polymer in another one can be observed in situ. The diffusion of each polymer can then be followed independently, provided that the compounds have some infrared distinguishable absorption bands. It is possible to work in a broad range of temperatures (below and above the T_g) and with a wide variety of interface combinations (amorphous, crystalline, thermoplastic, thermoset polymers, different molecular weights, etc). The ATR method offers the advantage of measuring the diffusion coefficients over a wide range of values: $10^{-5} - 10^{-16} \text{ cm}^2\text{sec}^{-1}$, as well as characterizing chemical interactions occurring within the polymeric system.

3.1.1.2. Optical principles of ATR spectroscopy

Harrick and others have presented the fundamental principles of Attenuated Total Reflectance (ATR) spectroscopy in detail. The ATR technique requires an internal reflection element (IRE), also called the denser or propagating medium, and often referred to as the ATR crystal. The sample, called the rarer medium, because of its lower refractive index, is in contact with this crystal. Thus an absorbing medium is in contact with a reflecting one. As shown in Fig.3.4, an incident beam enters the ATR crystal from one of the side faces and is totally

reflected at the interface with the sample. The beam then travels inside the ATR crystal and finally exits from the other side face.

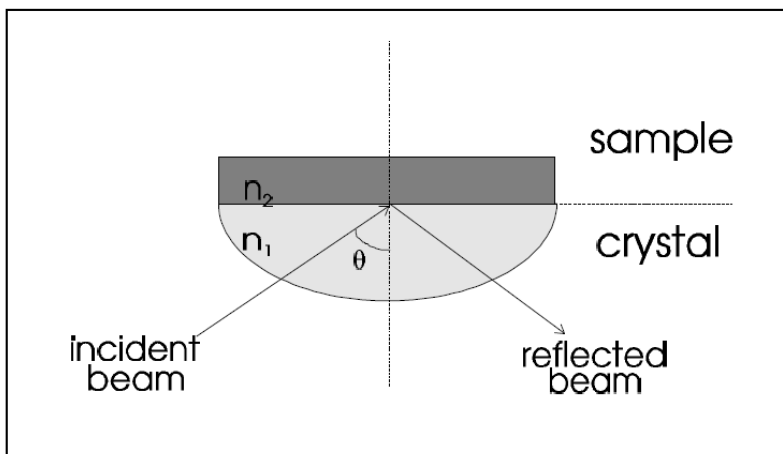


Fig.3.4. Schematic representation of total internal reflection

The nature of the interaction at the interface depends on the refractive indices of the ATR crystal and the sample, n_1 and n_2 respectively.

For an absorbing material, the refractive index is a complex quantity \tilde{n} , which is defined below:

$$\tilde{n} = n + i.k \quad (1)$$

where n is the real component of the refractive index (a constant at a particular frequency) k is the extinction coefficient, also called the absorption index. For organic materials in the mid-infrared region, the refractive index is usually about 1.5. The angle of incidence, θ , is defined as the angle with respect to the normal to the face of the IRE crystal.

Total internal reflection occurs only if $\theta \geq \theta_c$, where the critical angle θ_c is given by the equation:

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right) \quad (2)$$

where $n_1 > n_2$ so that $(n_2/n_1) < 1$, n_1 is the refractive index of the ATR crystal, n_2 is the refractive index of the sample. In order to avoid some distortions in the band shapes, the angle of incidence has to be maintained well above the critical angle.

When the infrared radiation is totally reflected at the interface between the crystal and the sample, an evanescent wave, which is the wave of infrared radiation inside the ATR crystal, penetrates a small distance in the sample. It represents the superposition of the incident and

reflected beams at the interface between the IRE and the sample. The total distance sampled by the evanescent wave is actually much longer than the so called penetration depth, which is defined as the distance at which the relative electric field is reduced by a factor e^{-1} .

Assuming a small extinction coefficient (the sample is a non-absorbing medium and $k = 0$ in the equation (1)), the penetration depth d_p in mm of the IR radiation is given by:

$$d_p = \frac{\lambda}{2\pi \cdot n_1 \cdot \sqrt{(\sin \theta)^2 - \left(\frac{n_2}{n_1}\right)^2}} \quad (3)$$

where λ is the IR wavelength of the light in free space in mm, $\lambda = (10,000/\sigma)$, where σ is the wavenumber in cm^{-1} , θ is the angle of incidence n_1 is the refractive index of the ATR crystal n_2 is the refractive index of the sample in contact with the ATR crystal

At $\theta \gg \theta_c$, the approximations made for deriving the penetration depth equation (3) are no longer valid since the denominator is equal to zero. Knowledge of the penetration depth is very important when working with solids since the chemical composition of solids can vary with depth. By changing the angle of incidence it is possible to study surfaces at various depths. The penetration depths can be calculated with the use of equation (3). From this equation, we see that d_p decreases as q increases at constant n_1 , n_2 , and λ . This is illustrated in Fig.3.5. for $n_1 = 2.42$ and $n_2 = 1.53$. On the other hand, d_p increases proportionally with λ at constant q , n_1 and n_2 , as demonstrated in Fig.3.6. for $n_1 = 2.42$ and $n_2 = 1.53$.

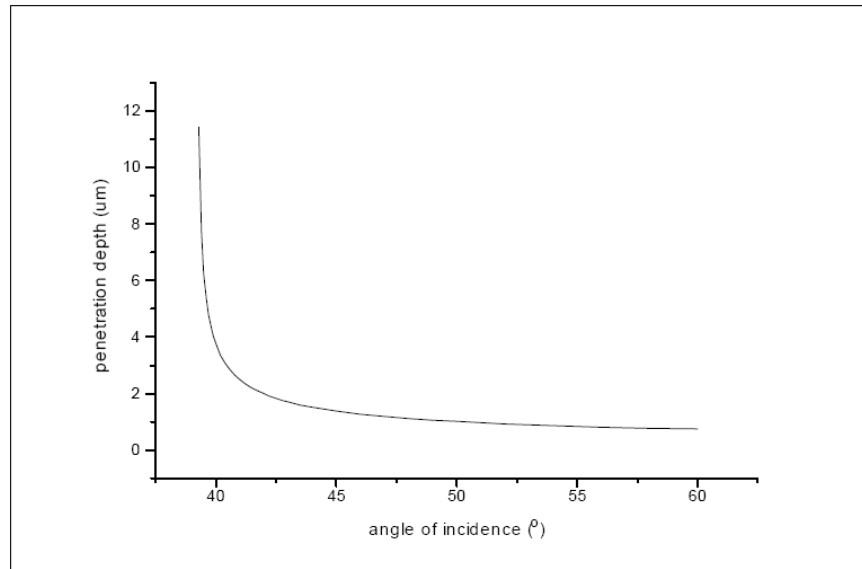


Fig.3.5. Penetration depth, d_p , versus angle of incidence q at 1507 cm^{-1}

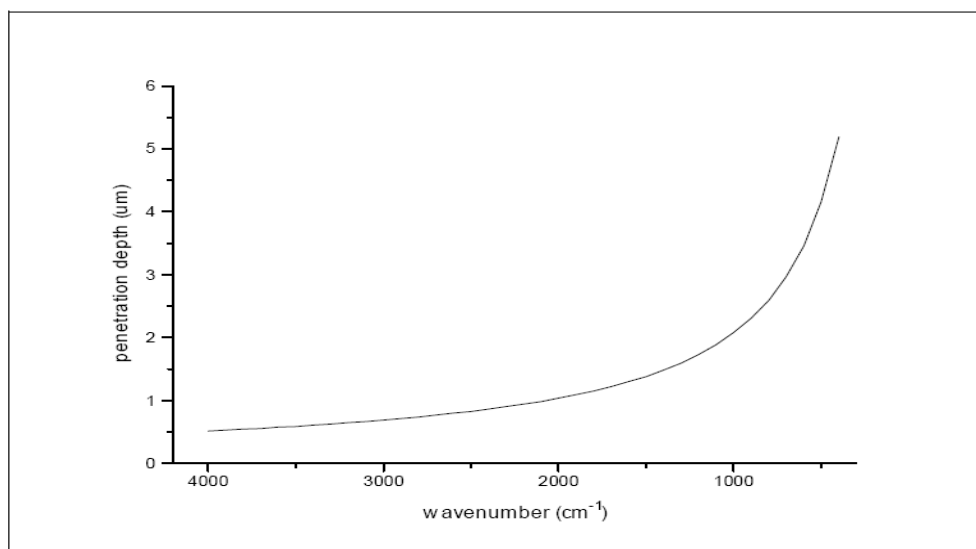


Fig.3.6. Penetration depth, d_p , versus wavenumber for $\theta = 45^\circ$.

As shown in Fig.3.7, the electric field magnitude E undergoes an exponential decay (the largest contribution to the absorption intensity comes, thus, from the material which is close to the surface), and the rate of decay is defined as:

$$E = E_0 \cdot e^{-\left(\frac{z}{d_p}\right)} \quad (4)$$

where E_0 is the electric field magnitude value at the (sample/ATR crystal),
 z is the distance from the (sample/ATR crystal) interface,
 d_p is the penetration depth.

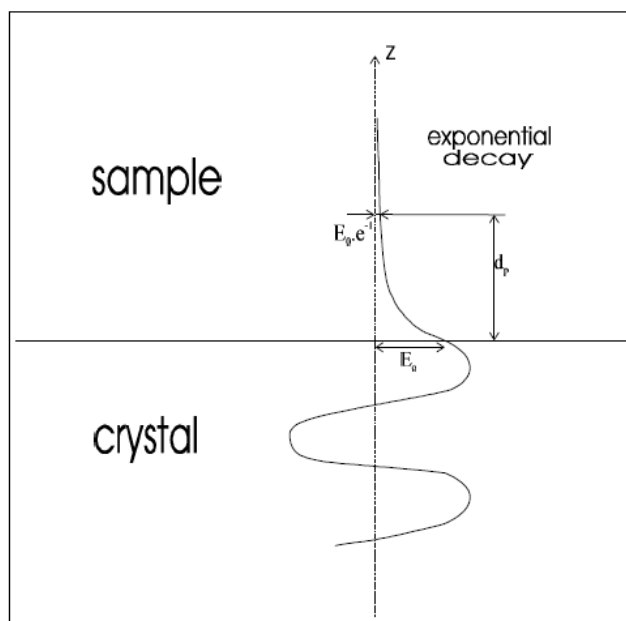


Fig.3.7. Schematic of the evanescent wave near the interface

The square of the electric field magnitude gives us its intensity, I , which can be related to the absorbance of light. To summarize, the sample is able to absorb light of that of the evanescent wave at particular wavenumbers. Some energy is, thus, removed from the reflected beam and hence, the name Attenuated Total Reflectance (ATR). The decrease in the reflected beam intensity results in an absorption spectrum. The spectrum can then be interpreted in terms of the physical and chemical structure and properties of the system.

3.1.1.3. Advantages of FTIR

- FTIR gives a much better spectrum because spectra are recorded in 30 seconds at a resolution of 8cm^{-1} .
- High resolution in FTIR is easier to obtain without sacrificing sensitivity.
- FTIR may be used to examine solid polymeric samples of an intractable nature.
- FTIR spectrometer may be used to obtain spectra from trace amounts of materials by depositing the material on a micro crystal.
- Response time is much more rapid FT than in dispersive spectroscopy. A large amount of energy is used quickly in FT as compared to a small amount of energy used slowly in other spectroscopy.
- The accuracy in wavenumber measurements is same over the whole range in FT instrument.
- FTIR is especially useful for examining small samples (several scans can be added together).

3.1.2. Alternating DSC (ADSC) or modulated temperature DSC

3.1.2.1. Principle

Modulated temperature differential scanning calorimetry (MTDSC) is thermo analytical technique which involves superimposition of a modulation on the conventional linear heating, cooling or isothermal temperature program. The temperature modulation can be described by sinusoidal function (Fig.3.8(a)), linear saw-tooth pattern (Fig.3.8(b)) or some other mathematical expression.

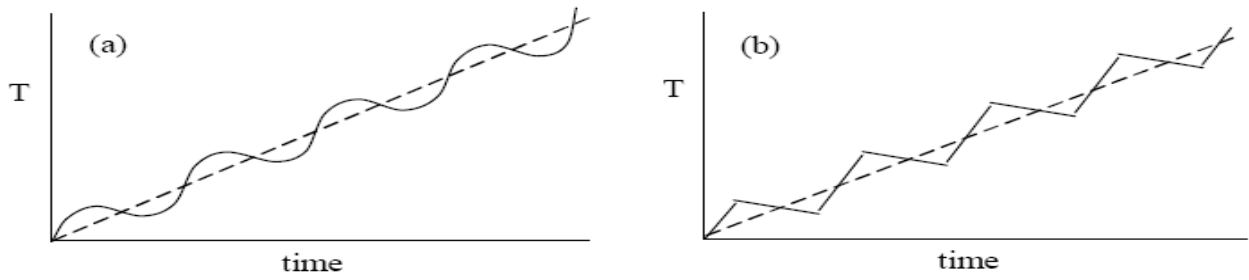


Fig.3.8. (a) Sinusoidal function and (b) linear saw-tooth pattern

A discrete Fourier transformation of the modulated heat flow (raw signal) yields the dynamic heat flow (Φ_d) and deconvoluted (average) response (Φ_{dc}). The latter is denoted as total heat flow. It can be separated into its heat capacity and kinetic components, also known as reversing (Φ_{rev}) and non-reversing heat flow (Φ_{non}), respectively. Another possibility of interpretation of the results is enabled by calculation of complex heat capacity (C_p^*), which represents the ratio of the modulated heat flow amplitude and modulated heating rate amplitude. C_p^* consists of storage or in-phase heat capacity (C_p') and loss or out-of-phase heat capacity (C_p''). Reversible responses (like glass transition) are reflected on the C_p' curve. Therefore storage heat capacity can be compared to reversible heat flow signal [38].

ADSC is based on the temperature modulation during a constant heating rate in the non-isothermal experiments, but the quasi-isothermal conditions mean that the temperature is altered in a sinusoidal fashion with an angular frequency ω (radian s^{-1}) and sufficiently small amplitude A_T about a constant temperature T_0 . In general, it follows:

$$T = T_0 + q_0 t + A_T \sin(\omega t),$$

$$\omega = \frac{2\pi}{t_p}$$

where T_0 is the initial temperature, q_0 is the underlying heating rate which is zero in isothermal experiments and t_p is the period. These three heating - related experimental variables (q_0 , A_T , ω) may be used to improve DSC results.

Schawe defined a complex heat capacity as:

$$C_p^* = C_p' - iC_p'',$$

where C_p' is the real (in-phase) component, and C_p'' the imaginary (out-of-phase) component. This definition of C_p^* shows the connection of the heat capacity with time-dependent molecular movements. The real part of the heat capacity describes molecular motions. The imaginary part is linked to dissipation.

The general precautions that are necessary to ensure reliable and accurate results are careful sample preparation, appropriate sample size, use of adequate pans and purge gas, selection of appropriate purge gas flow, calibrations carried out under conditions identical to those used for sample measurement, etc. and it is strongly important to choose an optimized set of MTDSC parameters - the underlying linear heating rate (β), the temperature modulation amplitude (T_a) and the temperature modulation period (t_p). ADSC was performed in DSC-821 (METTLER, TOLEDO).

3.1.2.2. Advantages of ADSC over DSC

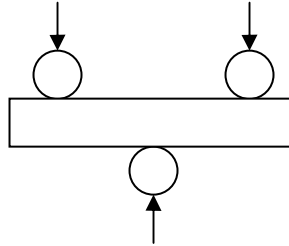
- Enhancement of both sensitivity and resolution in the same experiment
- Analysis of complex overlapping transitions
- Direct measurement of the heat capacity
- Detection of weak glass transitions

3.1.3. Short Beam Shear Test

It is one of the most popular flexural test methods. In this test the flat specimen is simply supported at the two ends and is loaded by a central load. Generally the flexural strength is obtained by measuring the applied load and corresponding strain. In this case we are obtaining the interlaminar shear stress values. The most widespread method of testing ILSS is the short span flexural test. If despite the short span to thickness ratio, the specimen fails in the flexural rather than a shear mode, the result of the test should not be reported as ILSS. Short span flexural testing is applicable to composites with unidirectional and bi-directional reinforcement, but does not give satisfactory results with planer random and three dimensionally random short fibre composites.

$$ILSS = 0.75p/bt$$

It shows the set up of three point bend test. Here the specimen is simply supported at the two ends and is loaded by a central load. Below is given the formula to obtain the ILSS value. Where p is the load at yield, b is the width of the sample and t is the thickness of the sample.



ILSS data are often used to specify the quality of the composites. It is considered as a direct function of interfacial adhesion.

3.1.4. SEM Test

Fractography” has become synonymous with an investigation in which both the mechanics of cracking are identified and the influence of the environment and/or the internal structures of the component on the mechanics of fracture are determined.

Examination of the fracture surface of a polymer is usually carried out sequentially using low power optical microscopy, high power optical microscopy, and either scanning electron microscopy SEM applied directly to the surface or transmission electron microscopy TEM of replicas taken from the surface. The use of replicas has declined in the recent years due to the improvement and increased availability of scanning electron microscopes. The scanning electron microscope SEM, due to its very large depth of field, is ideally suited to the study of fractures in polymers and can focus on even the most fibrous fracture surfaces. Magnifications between 20× and 10,000× are possible and it allows correlation of the detailed structures observed at high magnification with the coarser optically visible features of the fracture.

To understand the interfacial bonding condition between the fibre and the matrix and its effect on mechanical properties, photomicrographs were taken using a scanning electron microscope. Dramatic changes in the structure and properties of the composite when exposed to cryogenic temperatures, particularly in cyclical fashion, can be seen by studying the SEM micrographs. Generally cryogenic cycling leads to microcracking, delamination and potholing

that are localized surface degradation [39]. Increased thermal stresses are the underlying cause of microcracking in composites at cryogenic conditions. As the temperature of the laminate falls below its stress free temperature, residual stresses develop in the material. These stresses are the result of difference in coefficient of thermal expansion between the fibres and the matrix. As the temperature deviates from the stress free temperature, the amount of thermal stresses increases. And when these residual stresses become large enough they are relieved through physical processes such as microcracking, delamination and potholing.

3.2 MATERIALS AND EXPERIMENTAL

3.2.1. Materials

The unmodified epoxy resin (Araldide LY-556) based on Bisphenol-A and hardener HY-951 an aliphatic primary amine (Ciba-Geigy) used as matrix and glass fibre was used for preparing the micro-composites for hygrothermal treatment. The same test was conducted with another matrix i.e. unmodified polyester resin. For cryogenic treatment laminated composites were prepared from woven and chopped glass fibre for ILLS testing. The fibre used was E-glass fibre treated with silane-coupling sizing system (Saint-Gobian Vetrotex).

3.2.2. Experimental

3.2.2.1 Hygrothermal Treatment

The specimens were fabricated using the conventional hand lay-up method. A plane mould was treated with silicon based releasing agent for easy removal of glass/epoxy micro-composites. A single strand of glass and carbon fibre was placed on the mould and the layer of catalyzed epoxy was poured on to it uniformly. Very light rolling was then carried out to remove any gas pockets if present and to uniformly distribute the epoxy resin through out the composite. The micro-composites prepared were then cured at room temperature for 24 hours. Then the samples were treated in microprocessor controlled Brabender climatic chamber for hygrothermal conditioning. The samples were divided into six batches, they were hygrothermally treated for 10, 20, 30, 40 and 50 hours in 95% RH and one batch remain untreated.

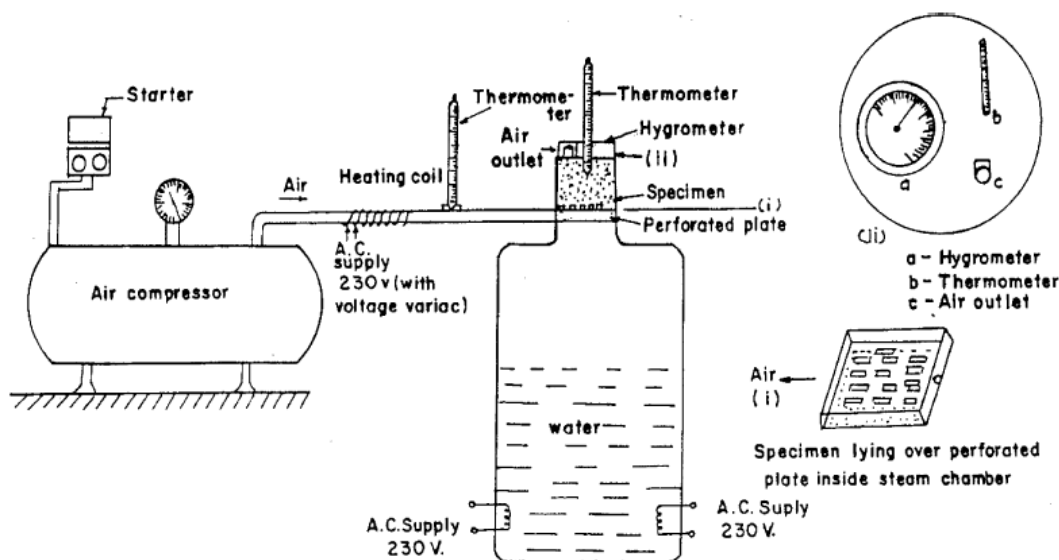


Fig.3.9. The schematic diagram of microprocessor controlled Brabender climatic chamber for hygrothermal conditioning

3.2.2.2. Cryogenic Treatment

The chopped and woven glass fibre/epoxy composite laminates were fabricated by wet lay-up method; the chopped and woven glass fibre cloth of required dimension was laid over a mould and then catalyzed epoxy resin was poured absorbed over the reinforcement. The wet composite was rolled, to distribute the resin and to remove the air pockets. The sequence was repeated until the desired thickness was obtained. The layered structure was allowed to harden on cure. It was cured at room temperature for 48 hours. After curing, the laminate was cut into the required size for 3-point bend (Short-Beam Shear) test by diamond cutter. Then stability test was done for the composite laminates. Here the laminates were weighed and then heated in an oven at 50°C. The weight is intermittently checked till we get a stable weight, that is, with further heating there is no change in the weight of the composite.

3.2.2.3. FTIR spectroscopy analysis

FTIR analysis was performed in FTIR spectrophotometer interfaced with IR microscope operated in reflectance mode. The microscope is equipped with a video camera, a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a computer controlled

translation stage, programmable in the x and y directions. The spectra were collected in the 4000cm^{-1} to 650 cm^{-1} region with 8 cm^{-1} resolution, 60 scans and beam spot size of $10\mu\text{m}$ - $100\mu\text{m}$. The spectral point-by-point mapping of the interface of the epoxy cured composites was performed in a grid pattern with the use of computer controlled microscope stage. Since the surface of the film was not perfectly smooth and its thickness was not uniform care should be taken to mount the sample such that a major portion of the plane was in the same focal plane. The FTIR imaging was performed in AIM-800 Automatic Infra red Microscope (SHIMADZU).

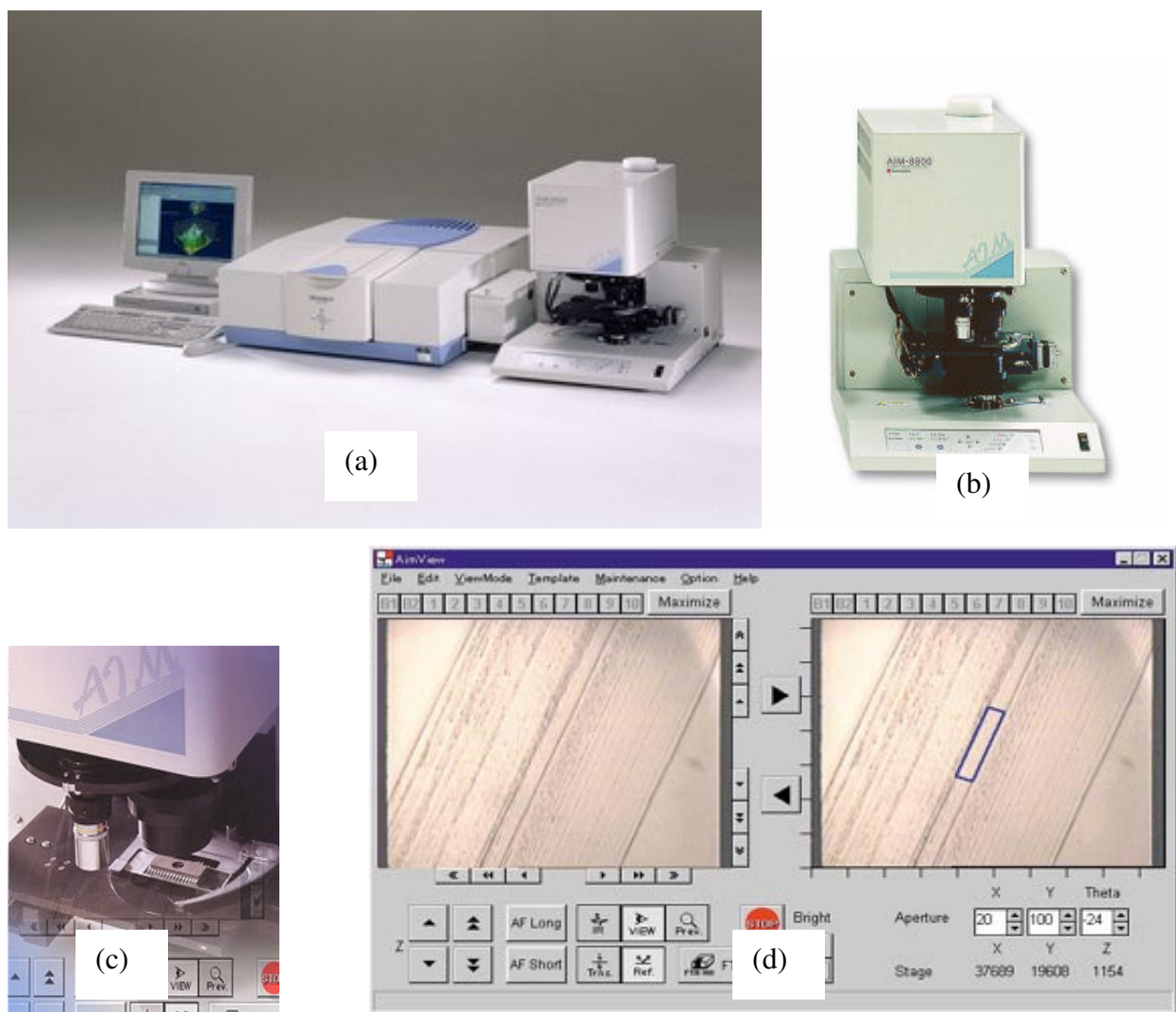


Fig.3.10. (a) FTIR spectrophotometer, (b)-(c) AIM-800 Automatic Infra red Microscope, (d) 2-D view taken by the microscope equipped video camera.

There are certain limitations of refraction and reflection at the fibre surface in the spectroscopy that will finally affect the FTIR spectra of glass/epoxy composites. Due to this only a small percent of light reaches the detector. It is difficult to separate these optical effects from the samples. However these optical effects can be minimized by taking FTIR spectra over the same region of the micro-composites.

3.2.2.4. ADSC analysis

The DSC measurements were performed on a Mettler-Toledo 821 with intra cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of $10^{\circ}\text{Cmin}^{-1}$ was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminum pans were used. The experiments were performed in the temperature range from 40°C to 100°C .



Fig.3.11. (a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) reference-sample chamber.

3.2.2.5. Flexural test (Short Beam Shear Test)

The short beam shear tests were carried out for first batch of samples immediately after exposure to cryogenic temperature. The former samples after exposure to room temperature and

the untreated as-cured samples were tested in short beam shear test at room temperature. All the mechanical flexural tests were performed at 2, 50, 100, 200 and 500 mm/min crosshead speeds. Then breaking load and strain at maximum load was measured from stress vs strain graphs for all the samples.

An Instron 1195 tensile testing machine was used to perform SBS tests in accordance with ASTM D 2344-84 standard. Multiple samples were tested at each point of experiment and the average value was reported.



Fig.3.12. Instron 1195



Fig.3.13. Short Beam Shear test set up, loading of the sample and fracture.

4. RESULTS AND DISCUSSION

4.1 Hygrothermal Treatment

Polymeric composites are used in many applications such as aircraft, supersonic jet, automotive materials due to its high specific strength, high stiffness and tailor able properties [40]. But in many applications they have the disadvantage of moisture absorption because of the large amount of hydroxyl groups in the structure which are susceptible to the polar water molecules which causes degradation in there mechanical, thermal and dielectric properties [41,42]. Moisture diffuses into the matrix of the composites and attacks the area near the interface due to its heterogeneous nature [17]. The coefficient of thermal expansion of glass fibre and epoxy are different so the moisture absorption causes differential volumetric expansion which leads to localized stresses and strain at the interface [19]. Moisture penetrates into the polymeric composites to lower the internal stresses and sometimes hygroelastic swelling of the polymer occurs to as the constituent macromolecules rearrange to relieve the osmotic pressure generated by the water molecules [3]. Moisture penetration is explained by many techniques in polymer composites. There are two main mechanisms involved first one is moisture diffusion into matrix and second mechanism is water diffusion along the fibre-matrix interface by capillary flow [5,16]. Water may be present in the polymeric composite material in dual phase i.e. either in the free molecules or/and clustered group [43]. It has been absorbed that absorption of moisture causes degradation of matrix-dominating properties such as interlaminar shear strength and in-plane shear strength and compressive modulus and fracture strength [44]. However in some cases in the initial sorption period the longitudinal strength increases, this may be due to reduced flaw size in the matrix as a result of plasticization [45].

4.1.1. Epoxy- glass fiber micro-composites

Chemical degradation includes matrix hydrolysis, interface hydrolysis and fibre degradation in some cases while physical degradation involves plasticization and swelling of the

matrix [46]. These effects are generally reversible when water is removed but high temperature exposure can produce irreversible effects which cause chemical degradation of the matrix and attack on the fibre-matrix interface [18]. Further there may be increase in internal voids, chain expansion and the micro-crack formation into the matrix. However in many cases in the initial sorption period glass transition temperature increases, this may be due to formation of double hydrogen bond in the epoxy matrix or at the interface [43]. This shows that moisture absorption is matrix dominating property in fibrous composites [7]. The structure near the interface is different from the bulk matrix so this leads to composite absorbing different amount of water per unit mass of resin than the bulk polymer [23]. The amount of water absorbed at the interface also depends upon nature of the glass surface, lower the functionality of the silane is higher the cross-link density at the interface and lesser will be the amount of moisture absorbed [47].

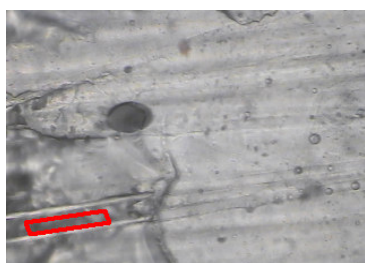
Moisture penetration at the interface contributes free volume of mesoscopic origin in addition with the one existing in the bulk of the matrix phase [48]. The performance of fibre-reinforced polymer composite is controlled by the adhesion chemistry at the fibre-matrix interface [49]. Low temperature conditioning improves the strengthening phenomenon due to mechanical keying at the fibre-matrix interface and at room temperature and high temperature act as a softening agent [15]. It was also reported that water at the interface causes replacement of covalent bonds between the siloxane backbones of the sizing material on the glass surface with strong hydrogen bonds between the glass surface, water molecules and the network of silane coupling agents [20]. This strong physical interaction can create region where larger area of fibre and matrix participate in adhesion process. Larger contact area allows better transfer of load between fibre and matrix and thus maintaining the strength.

In the present work, FTIR-imaging and DSC techniques were used to assess the interface of hygrothermally treated glass/epoxy composites. Since the interface is buried inside the composite material and they are nanoscopic in nature their characterization is complicated. So there are many difficulties encountered in physio-chemical analysis of interfaces [16,50]. But FTIR-imaging is a best instrument for the distinct characterization in particular region such as interface of nano-dimensions. Till now FTIR-imaging was used for determining the structural gradient at the interface in epoxy curing behaviour at a glass/ epoxy composites [23]. DSC technique was used to monitor the effect of hygrothermal treatment on the glass transition temperature. These two techniques are the best way to determine the chemical behavior of polymeric composites.

4.1.1.1. FTIR measurements

The OH stretching in polymeric materials occur in the range of $3400\text{--}3200\text{ cm}^{-1}$. The major difference in absorption of water occurs in 3450 cm^{-1} . With the increase of ageing treatment the intensity at 3450 cm^{-1} increased and peaks got broaden. OH band in IR spectra can be differentiated into three bands, 3610 (water hydrogen bonded with epoxy resin), 3450 (weak hydrogen bonded with epoxy resin and partially dissolved) and 3240 cm^{-1} (strong water- water hydrogen bonded or cluster of water) [50].

Fig.4.1(a) to 4.1(c) represents 2D micrographs taken by FTIR spectrophotometer and fig. 4.1(d) to 4.1(f) spectra of these micrographs of untreated glass/epoxy micro-composites at different region. In this there is chemical gradient of absorbance from the glass fibre to the bulk of the epoxy resin. The grey line (fig. 4.1(f)) shows the spectral region near the interface of the micro-composites and the blue line (fig. 4.1(e)) is the spectral region away from interface. Finally the green line (fig. 4.1(d)) represents the spectral region in the bulk of the micro-composites. During curing the epoxide groups are opened by the amine groups and this may lead to generation of hydroxyl group. Figure 4.1(g) represents the superimposed peaks from interface to the bulk phase. The OH absorbance in the bulk region is more than the interface region; this may be due to the varying degree of curing in the bulk region and at the interface. The difference in the curing rate is due to the gradient in the active amine/epoxy ratio from the glass fibre surface to the bulk of the epoxy matrix [23]. The explanation may be that some of the amine group must be reacted with the OH groups of the fibre at the interface and another reason is that the hardener i.e. ethylenediamine used is smaller in diameter than the DGEBA so it is expected to diffuse faster in silane coupling agent at the fibre surface rapidly.



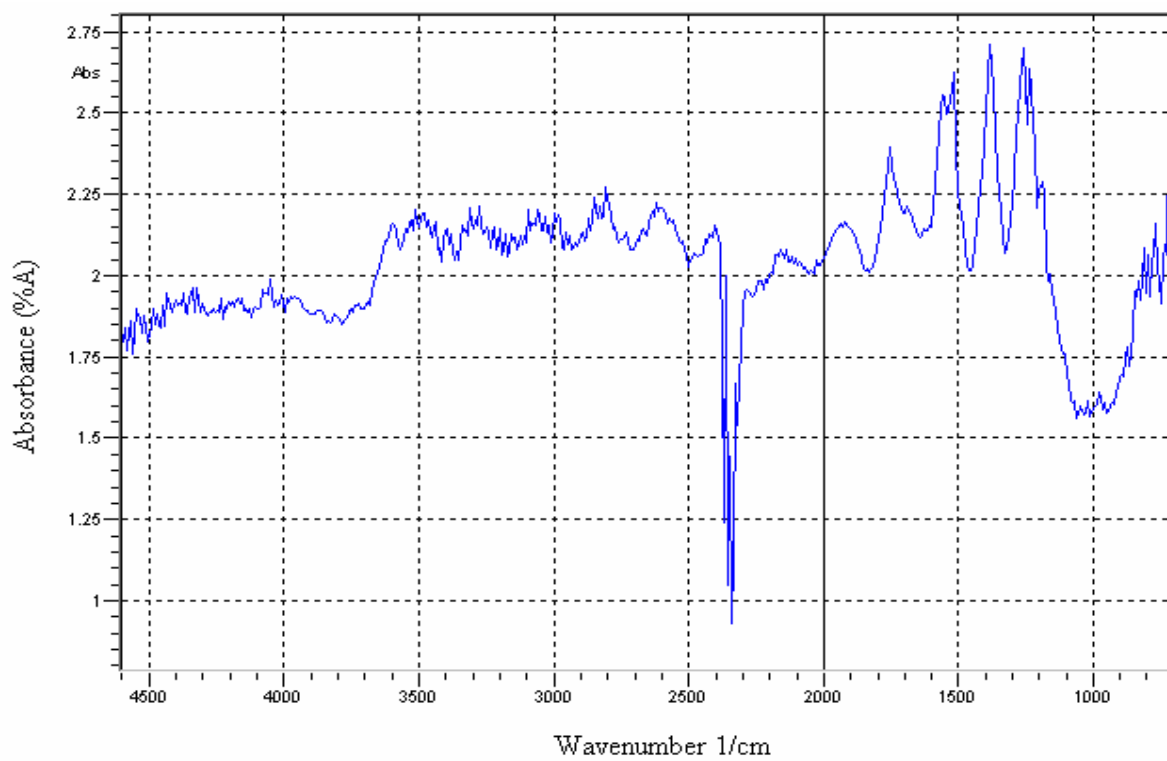
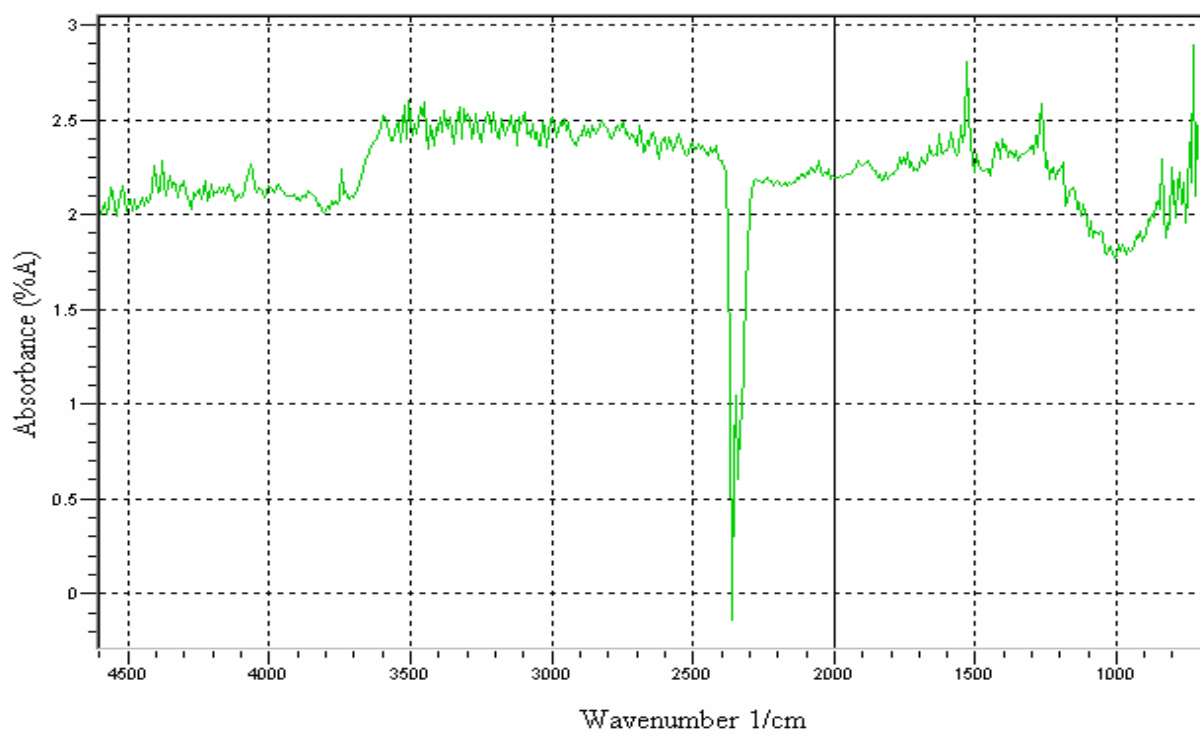
4.1.(a)

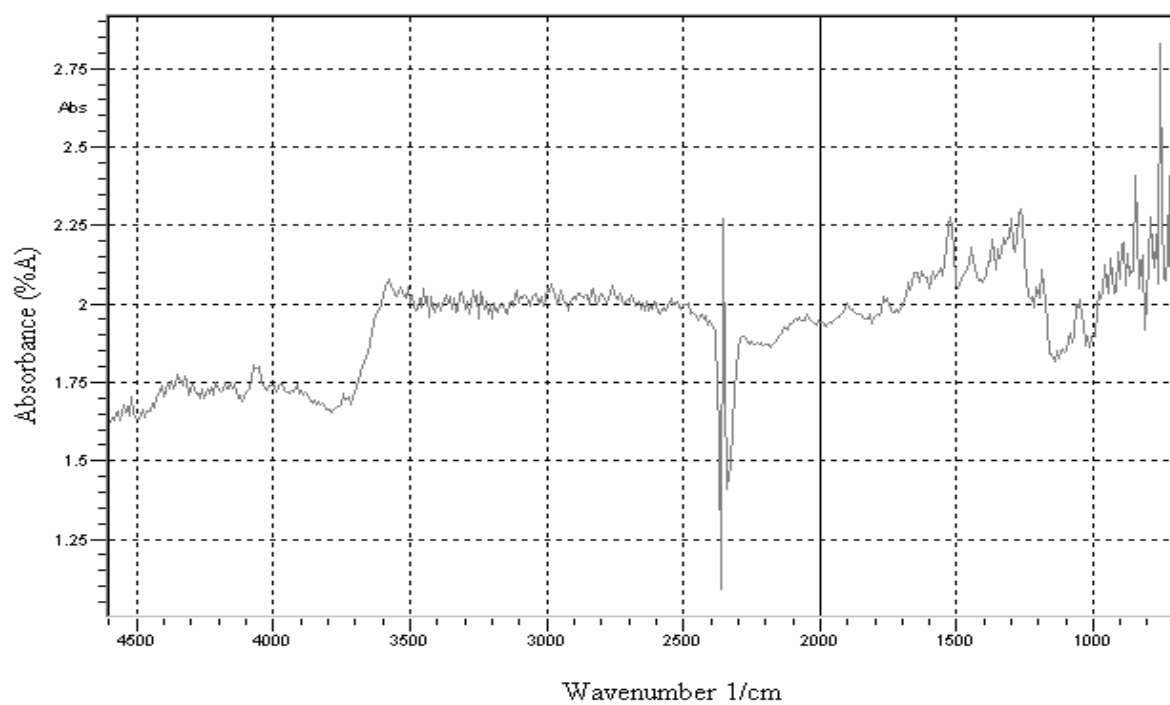


4.1.(b)

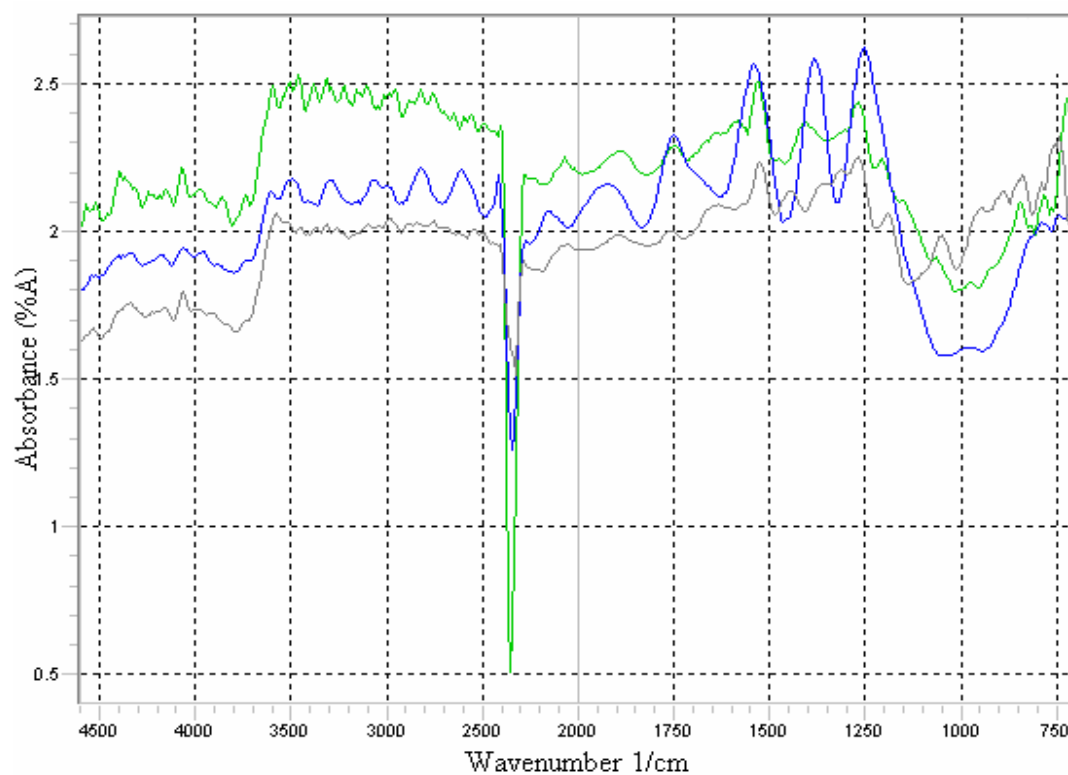


4.1.(c)





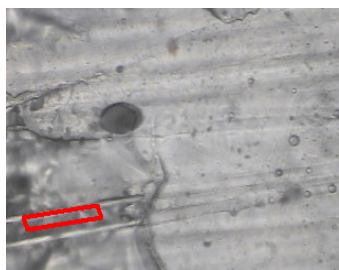
4.1.(f)



4.1.(g)

Fig.4.1. (a)-(c) The 2D micrograph taken by FTIR spectrophotometer, (d)-(f) there FTIR spectra and (g) the superimposed peaks for untreated glass/epoxy micro-composites from interface to bulk of the epoxy.

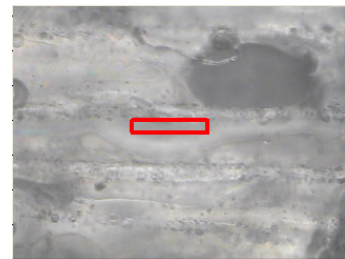
Fig4.2(a) to 4.2(f) represents 2D micrographs taken by FTIR spectrophotometer and fig. 4.2(g) to 4.2(l) spectra of these micrographs of hygrothermally treated at the glass/epoxy micro-composites. Figure 4.2 shows that FTIR spectra of hygrothermally treated sample at varying intervals of ageing hours of 10-50 hours. Figure 4.2(m) represents the superimposed peaks at the interface for the treatment of 10-50 hours. The spectra show that with the increase of hygrothermal treatment the intensity of the micro-composites increases. Since some of the epoxide groups at the interface was remained un-open due to incomplete curing the interface region is more prone to moisture absorption. The region which is mostly affected is centered on 3610 cm^{-1} [37]. The micro-voids may be formed during curing or stresses generated due difference in thermal expansion coefficient between the glass fibre and the epoxy matrix at the interface enhances the moisture absorption. Initially this moisture absorption increases the adhesion between the silane coupling agent and matrix by breaking the covalent bonds by strong double hydrogen bonds or shutting down the initial micro-voids formed by plasticization. But after long exposure moisture absorption may lead to debonding, delamination at the interface and plasticization which may decrease the glass transition temperature. However present work was focused on the initial moisture absorption and how they are increasing the properties of polymeric fibrous composite materials.



4.2.(a)



4.2.(b)



4.3.(c)



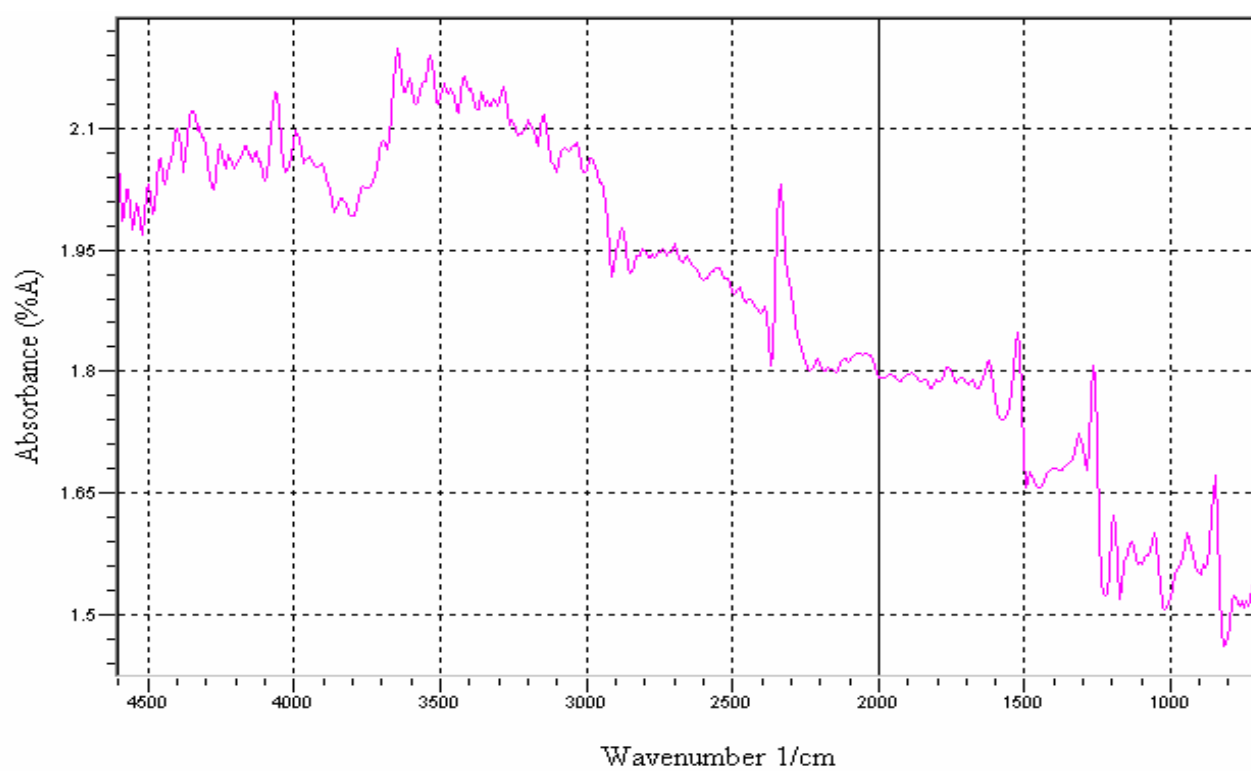
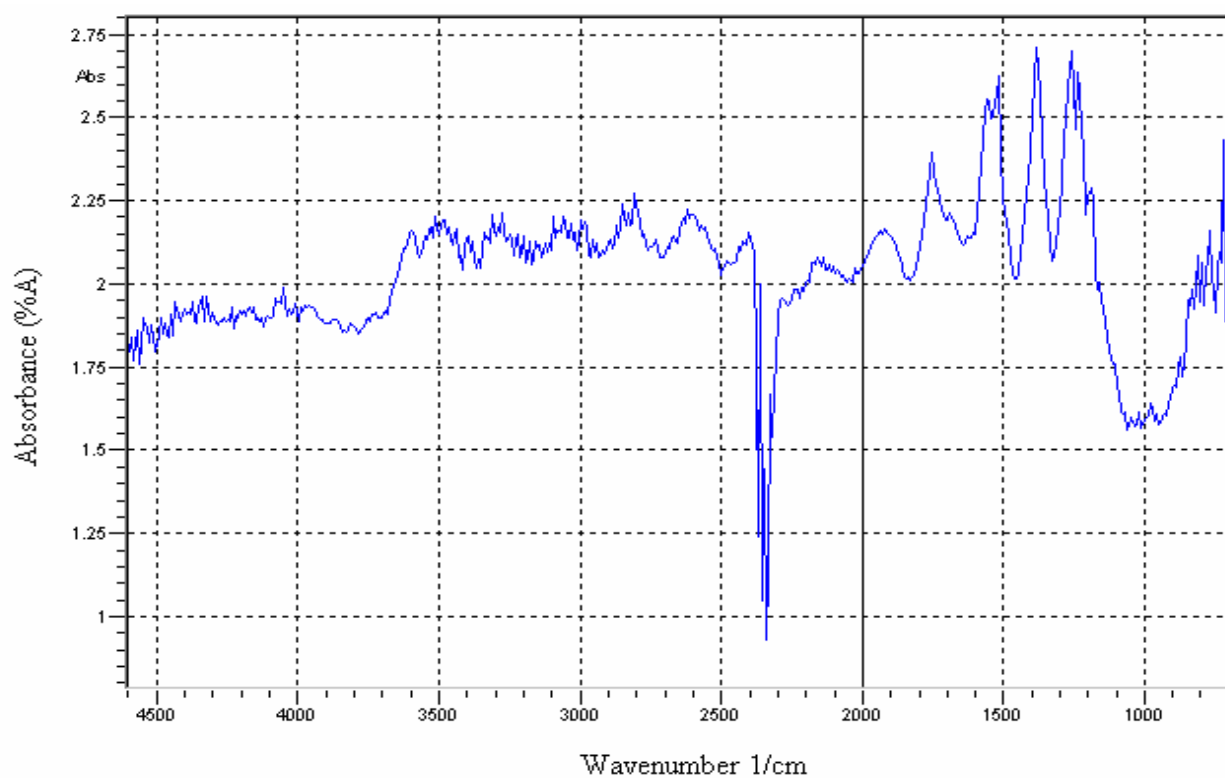
4.2.(d)

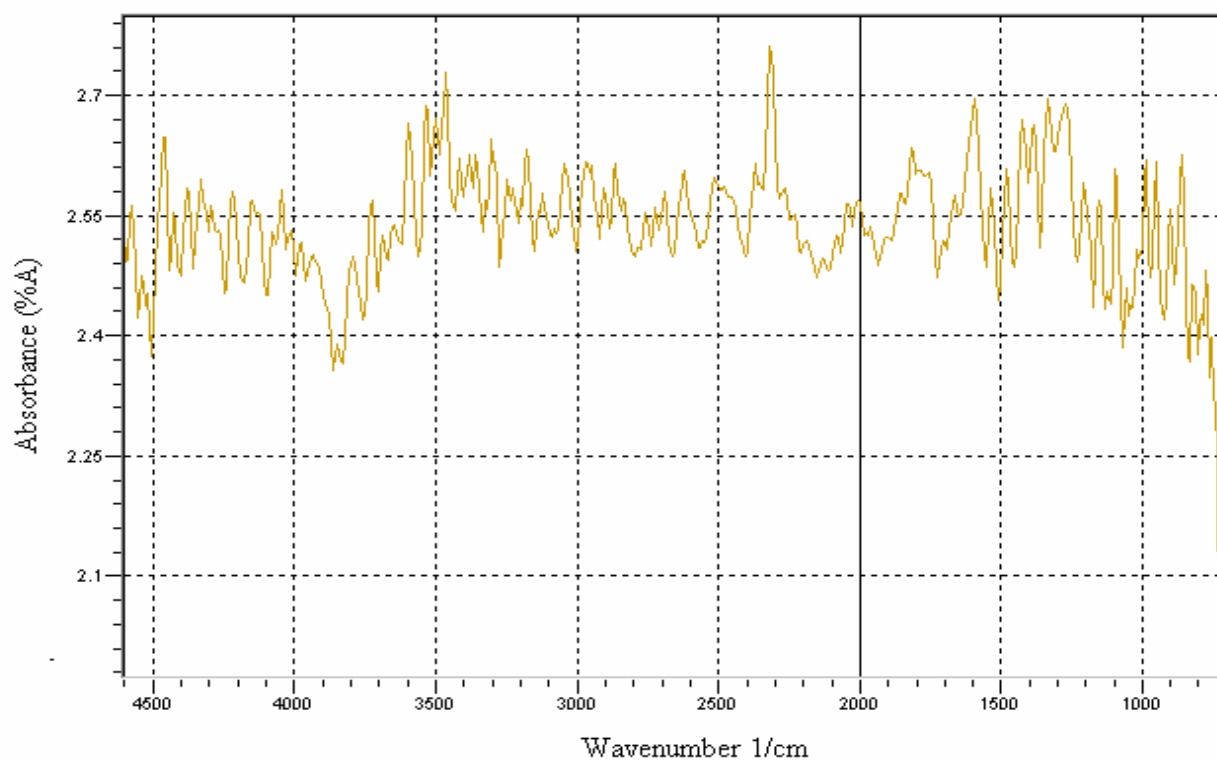
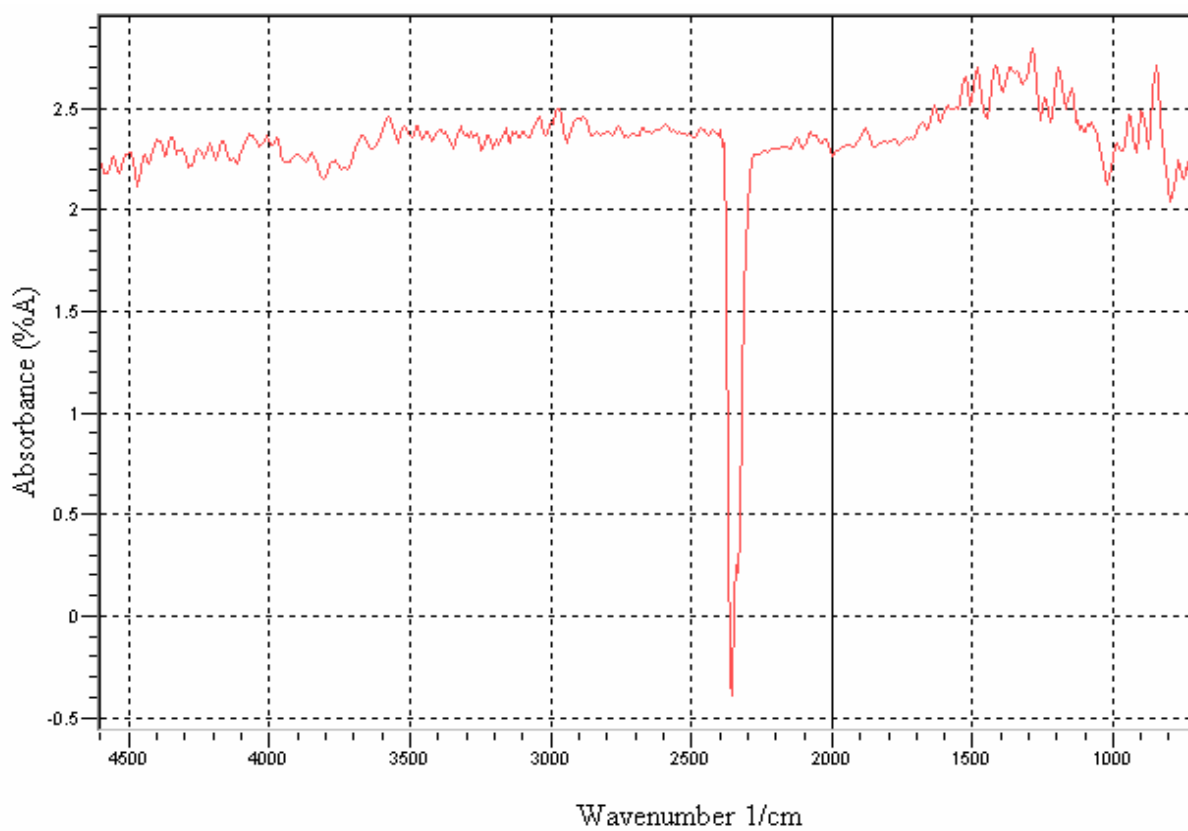


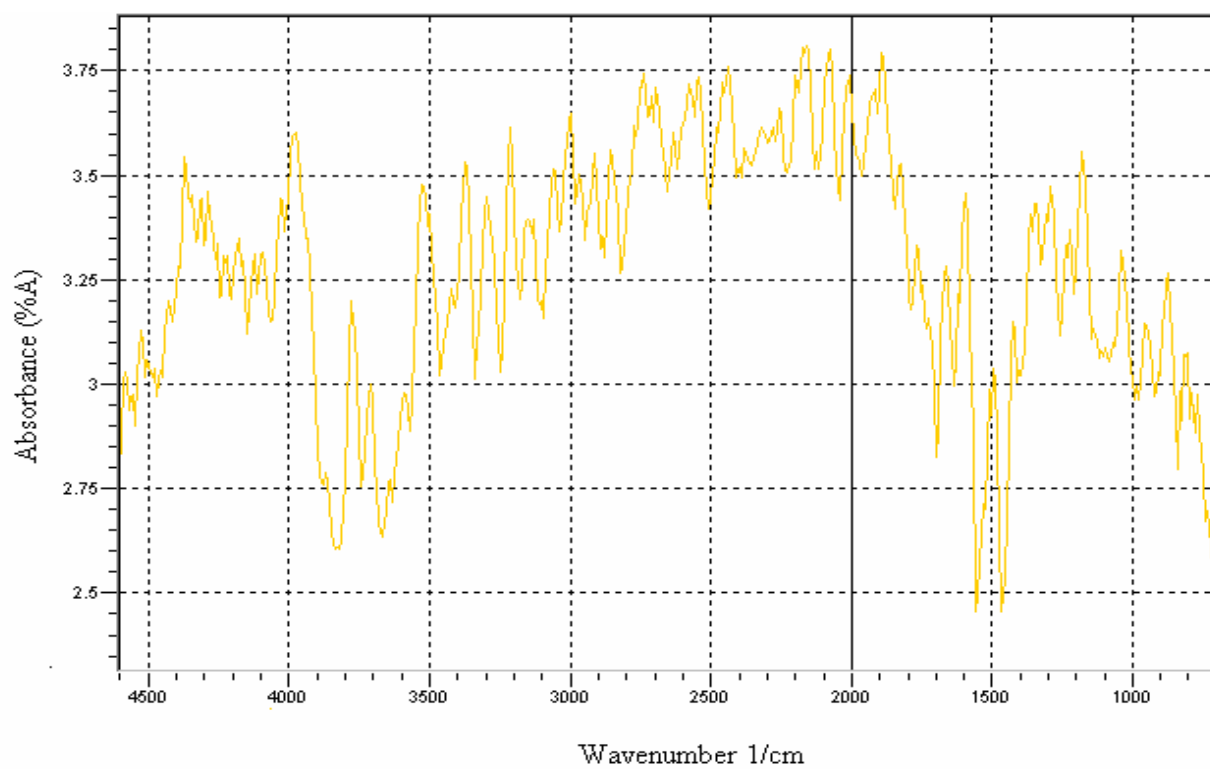
4.2.(e)



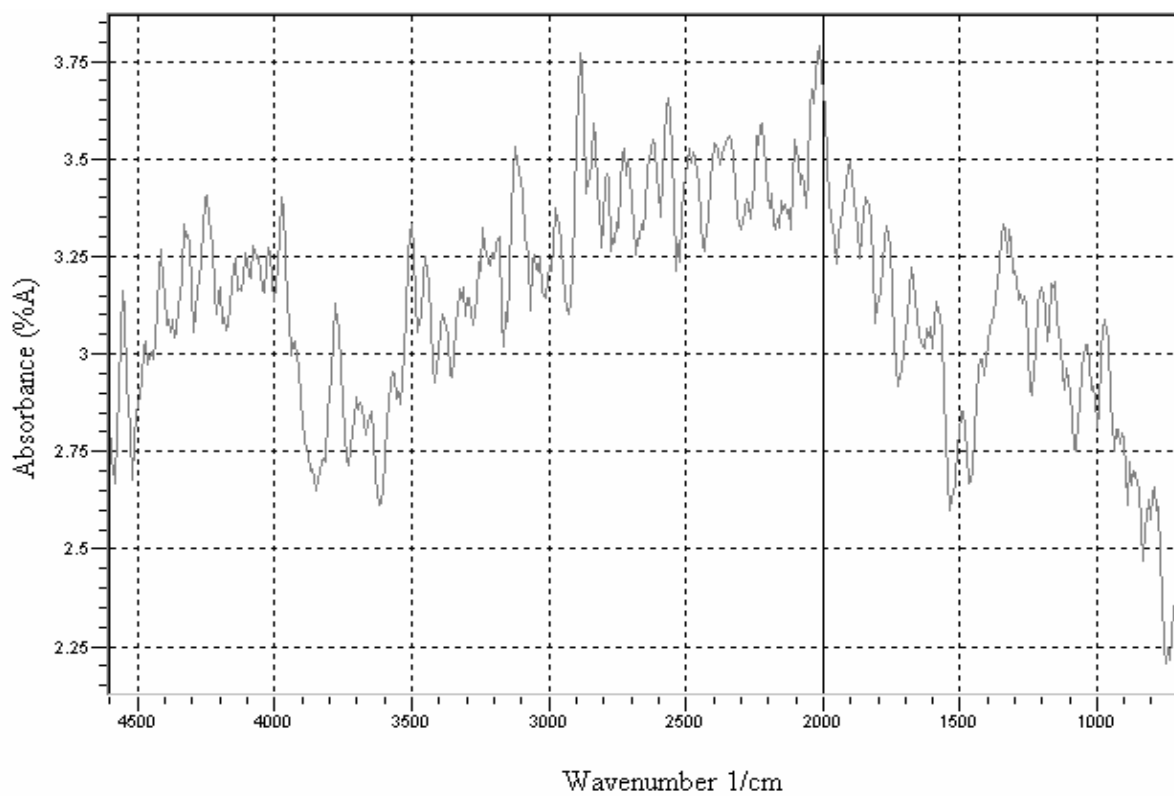
4.2.(f)



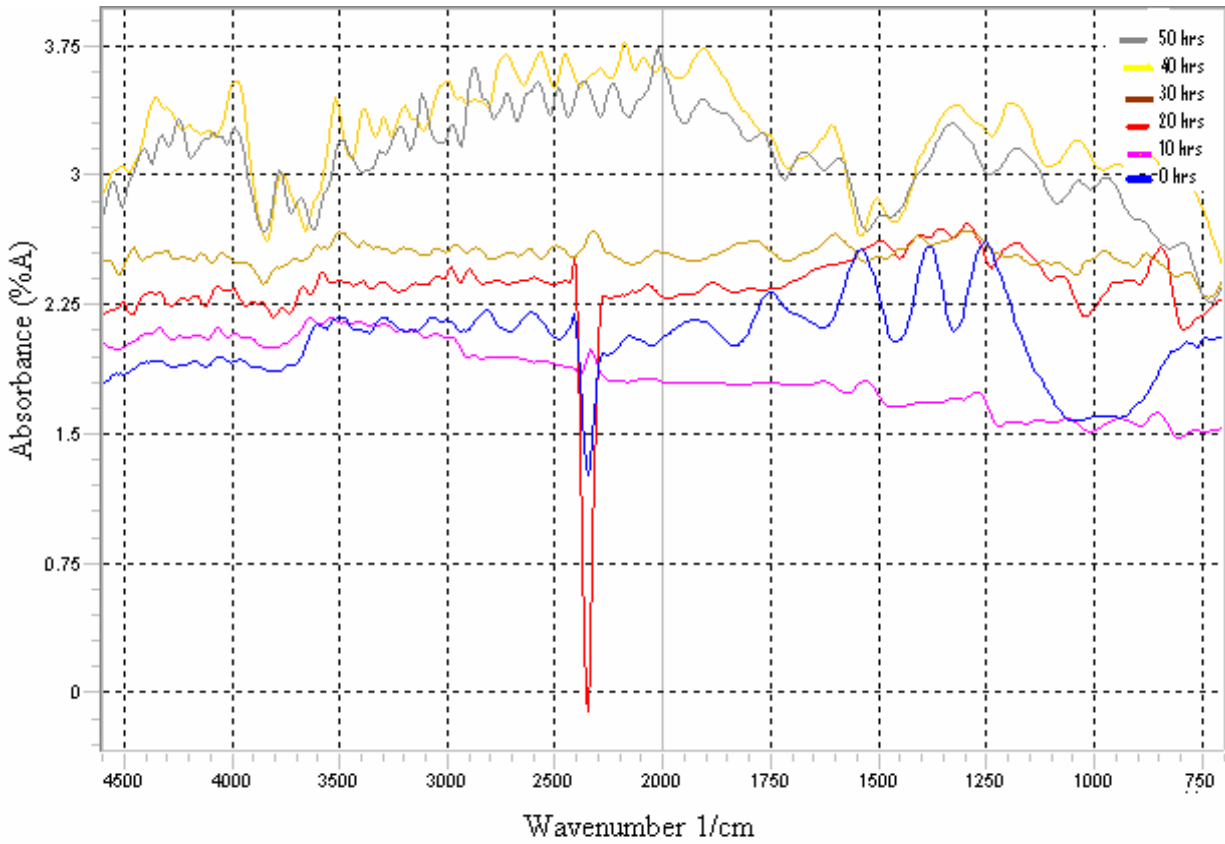




4.2.(k)



4.2.(l)



(m)

Fig.4.2. (a)-(f) The 2D micrograph taken by FTIR spectrophotometer, (g)-(l) there FTIR spectra and (m) the superimposed peaks for hygrothermally treated glass/epoxy micro-composites at the interface for the treatment of 10-50 hours.

4.1.1.2. DSC measurements

Fig.4.3 shows the effect of hygrothermal ageing on the glass transition temperature of glass/epoxy micro-composites. The measurement of glass transition temperature (T_g) is very important because it determines the critical service temperature of the polymer composites and finally their engineering application. They are used at a temperature below their T_g [51]. But when the polymeric composites are exposed to hygrothermal environment, the T_g usually decreases. In our case since the ageing time was very less so T_g increases. On the absorption of moisture water molecule will react with the hydroxyl group of the epoxy matrix and will forms a double hydrogen bond by replacing the covalent bonds with the silane coupling agent. If the

ageing time is increases the plasticization can take place and T_g will decrease which is generally observed in composites. This is still not clear that after what time plasticization effect come into picture. The formation of hydrogen bond can increase the moisture absorption, which is exothermic in nature. If the T_g increases the mechanical properties like interlaminar shear strength and fatigue strength increases [23].

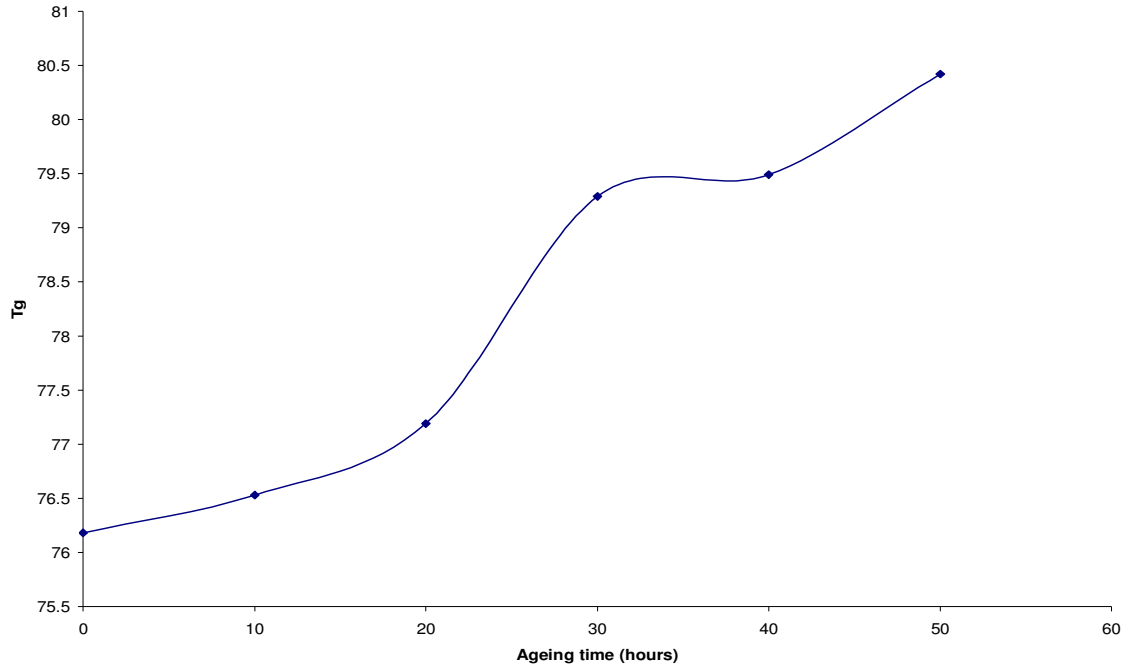


Fig.4.3. The glass transition temperature (T_g) at varying hygrothermal conditioning time.

4.1.1.3. Microscopic interface analysis

It was experimentally shown that if the moisture uptake is less the polymeric composites follow Fickian behavior. As the moisture content increases the non-Fickian behavior becomes more and more obvious [52]. However a 2-phase model of Carter and Kibler referred moisture diffusion as Langmuir-type [22]. The Fig.4.4 shows scanning micrographs of hygrothermally conditioned glass/epoxy micro-composites. The curing stresses generated at the interface can be relieved by the moisture absorption or moisture absorption may results into swelling stresses at the interface (Fig. 4.4a, 4.4b). The kinetics of moisture diffusion is a complex phenomenon. It is different for glass fibre and epoxy matrix and also depends upon their relative volume fraction, direction and type. Moisture penetration can cause matrix crazing (Fig. 4.4c) and since the

hygrothermal conditioning time was less it can only increase the interfacial adhesion by formation of strong hydrogen bond (Fig. 4.4d) and this may increase the load transfer from matrix to the fibre other through interphase region. This may further increase the mechanical properties of composites.

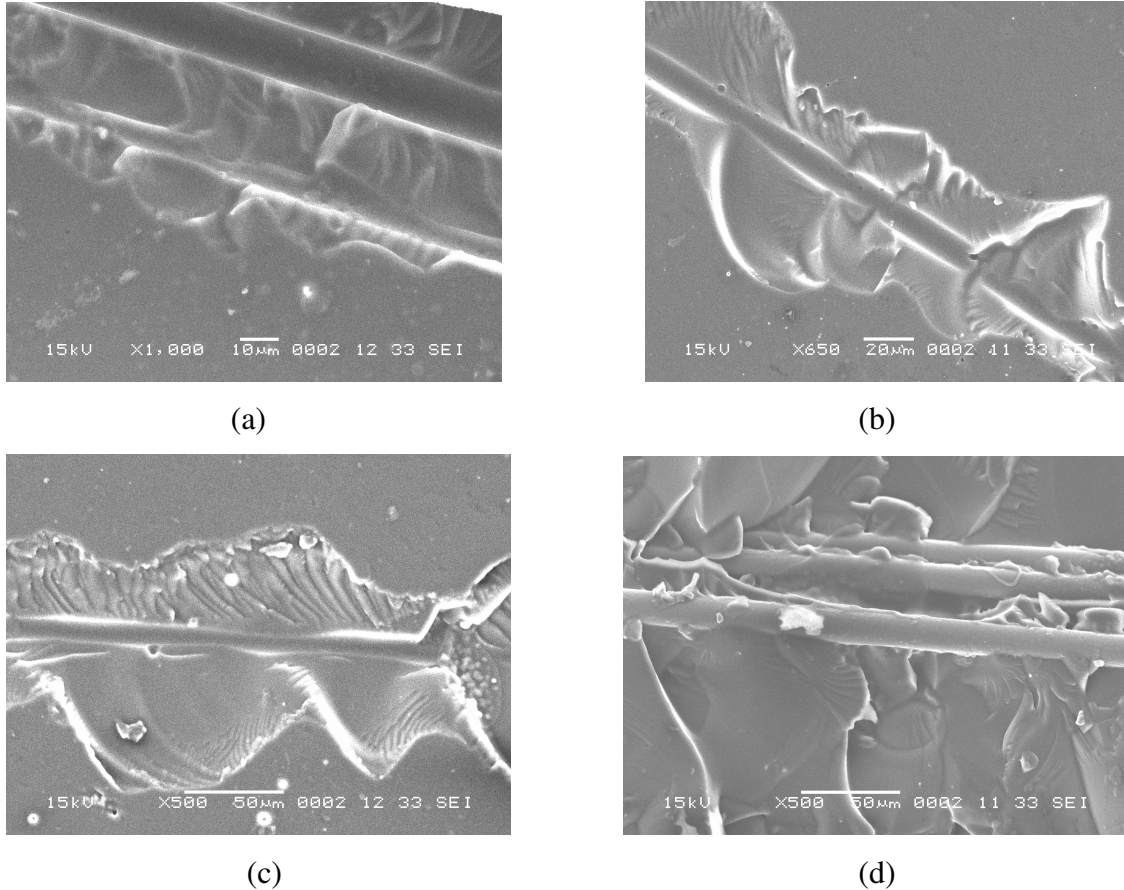


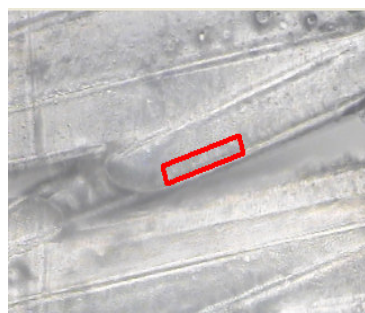
Fig.4.4 Scanning electron micrograph shows (a) stress field; (b) stress relaxation or swelling stresses generated; (c) matrix crazing; and (d) better adhesion at the interface in aged glass/epoxy micro-composites.

4.1.2. Polyester-glass micro-composites

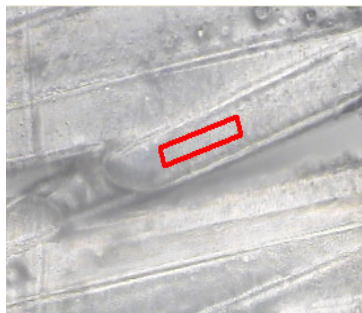
4.1.2.1. FTIR measurements

Fig.4.5(a) to 4.1(c) represents 2D micrographs taken by FTIR spectrophotometer and fig. 4.1(d) to 4.1(f) spectra of these micrographs of untreated glass/polyester micro-composites at different region. This figure also shows the similar type of spectra as observed in glass/epoxy

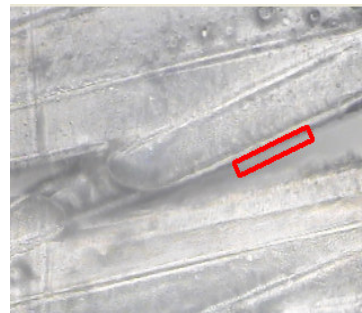
micro-composite system. This is the spectra of the fully cured sample without hygrothermal treatment. The grey line (fig. 4.5(d)) shows the spectral region near the interface of the micro-composites and the green line (fig. 4.5(f)) is the spectral region away from interface. Finally the pink line (fig. 4.5(e)) represents the spectral region in the bulk of the micro-composites. The intensity of OH absorbance is high for bulk region due to the higher curing than the interface region. Figure 4.5(g) represents the superimposed peaks from interface to the bulk phase.



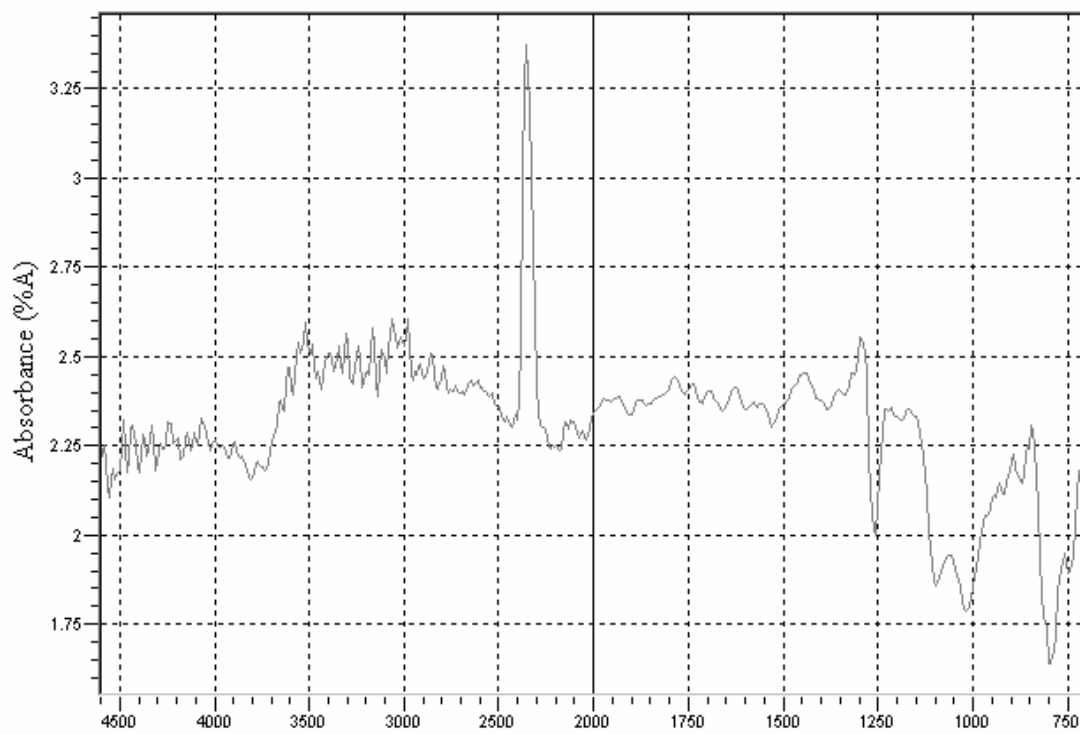
4.5(a)



4.5.(b)

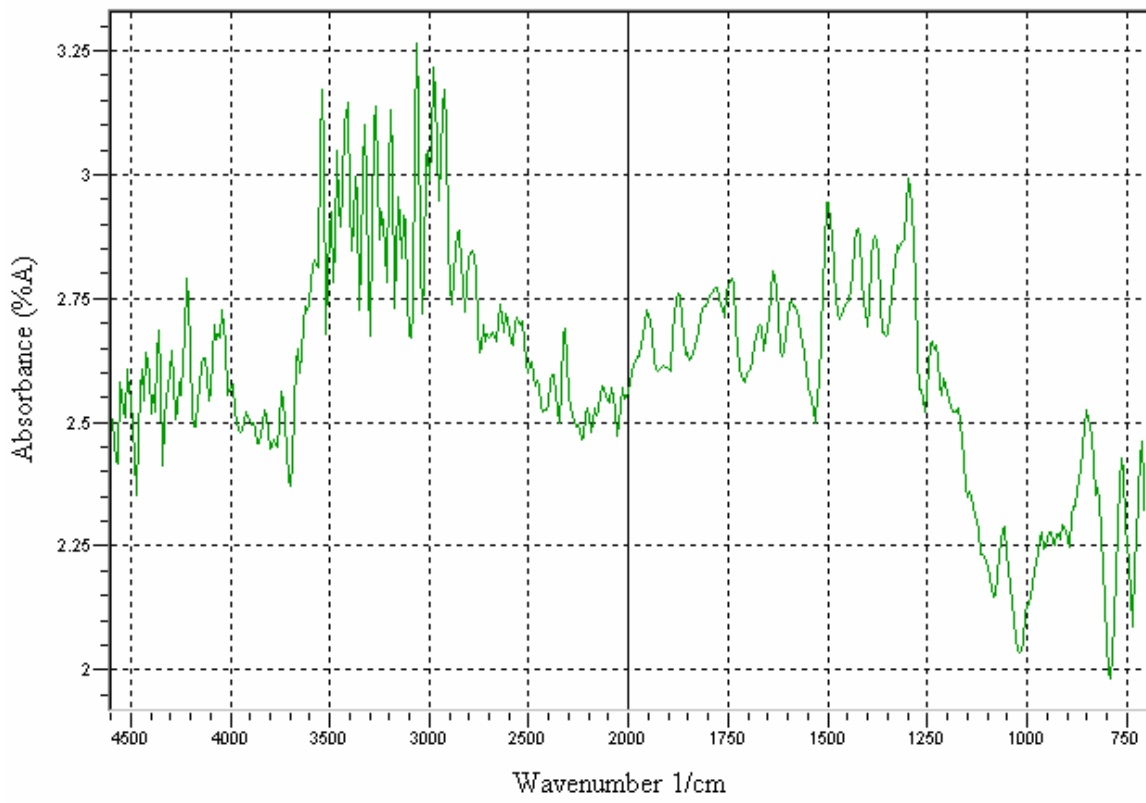
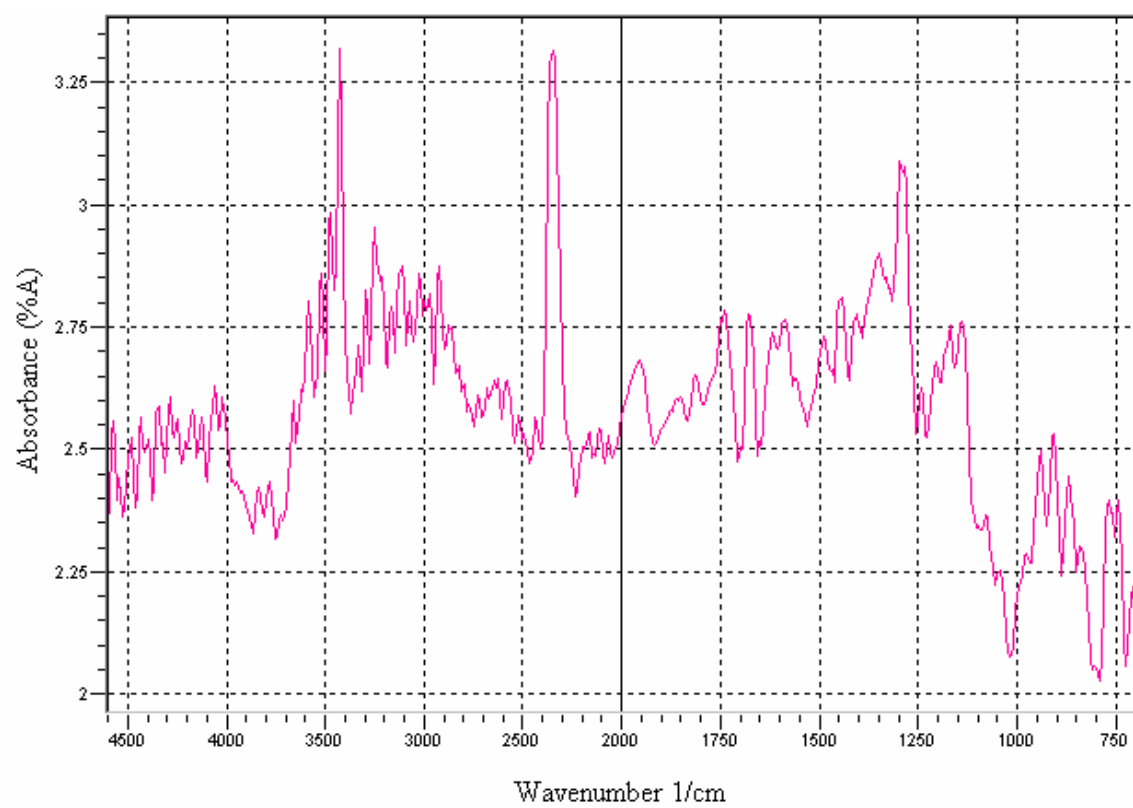


4.5.(c)



Wavenumber 1/cm

4.5.(d)





4.5.(g)

Fig.4.5. (a)-(c) The 2D micrograph taken by FTIR spectrophotometer, (d)-(f) there FTIR spectra and (g) the superimposed peaks for untreated glass/polyester micro-composites from interface to bulk of the polyester.

Fig.4.6(a) to 4.6(f) represents 2D micrographs taken by FTIR spectrophotometer and figure 4.5(g) to 4.5(l) spectra of these micrographs of hygrothermally treated at the glass/polyester micro-composites. Figure 4.2 shows that FTIR spectra of hygrothermally treated sample at varying intervals of ageing hours of 10-50 hours. With the increase of treatment hour the intensity near the OH absorbance range i.e. 3400cm^{-1} - 3200cm^{-1} increases as shown in the figures. This may also be due to the formation of double hydrogen bond at the interface of the fibre/matrix system or in the bulk phase.



4.6.(a)



4.6.(b)



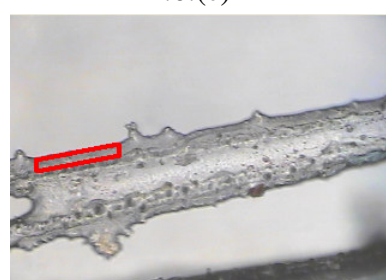
4.6.(c)



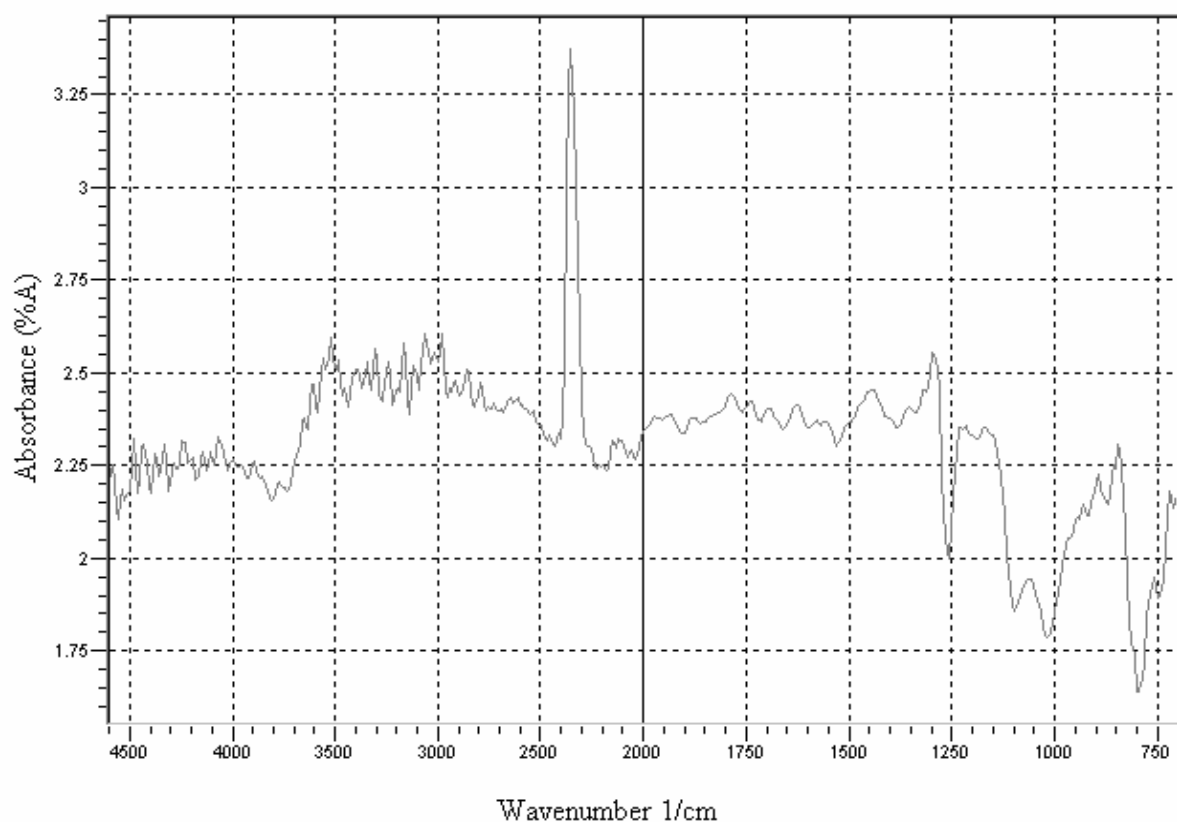
4.6.(d)



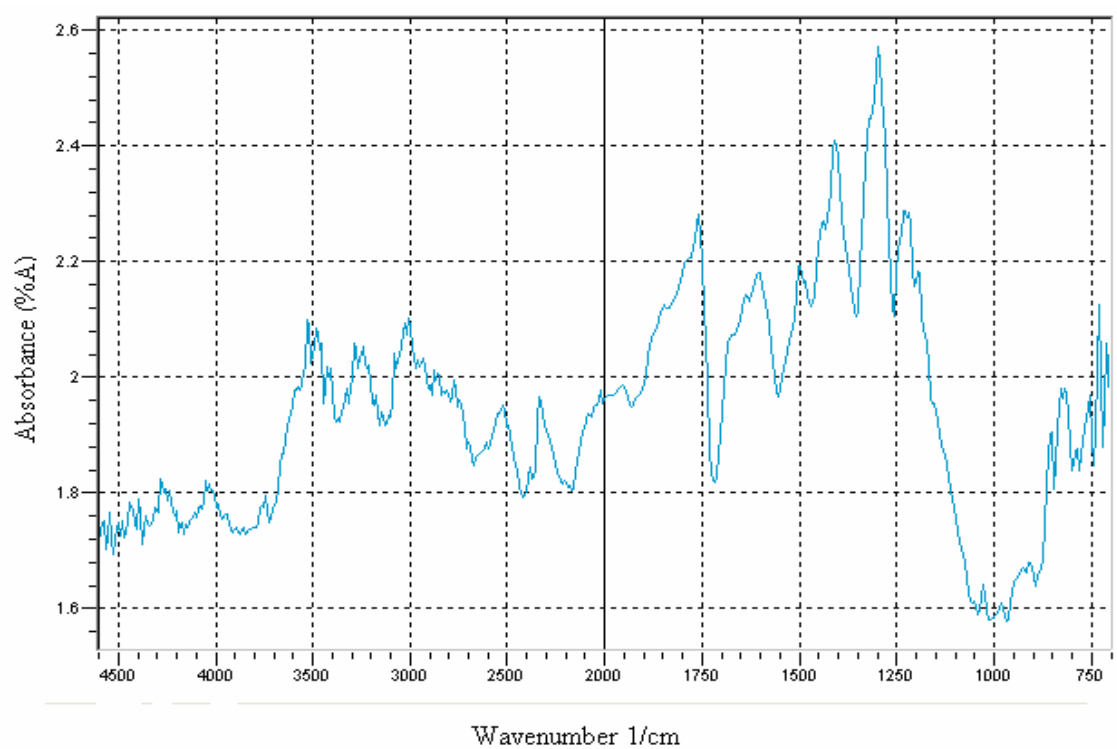
4.6.(e)



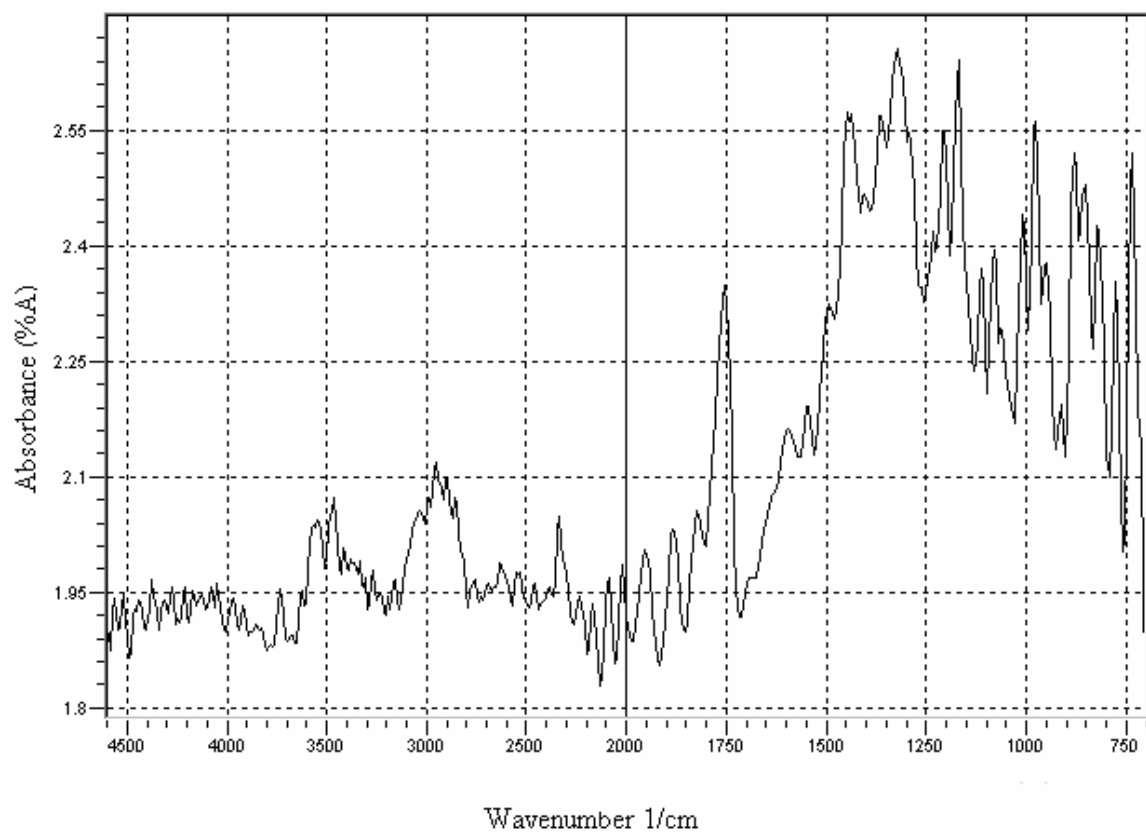
4.6.(f)



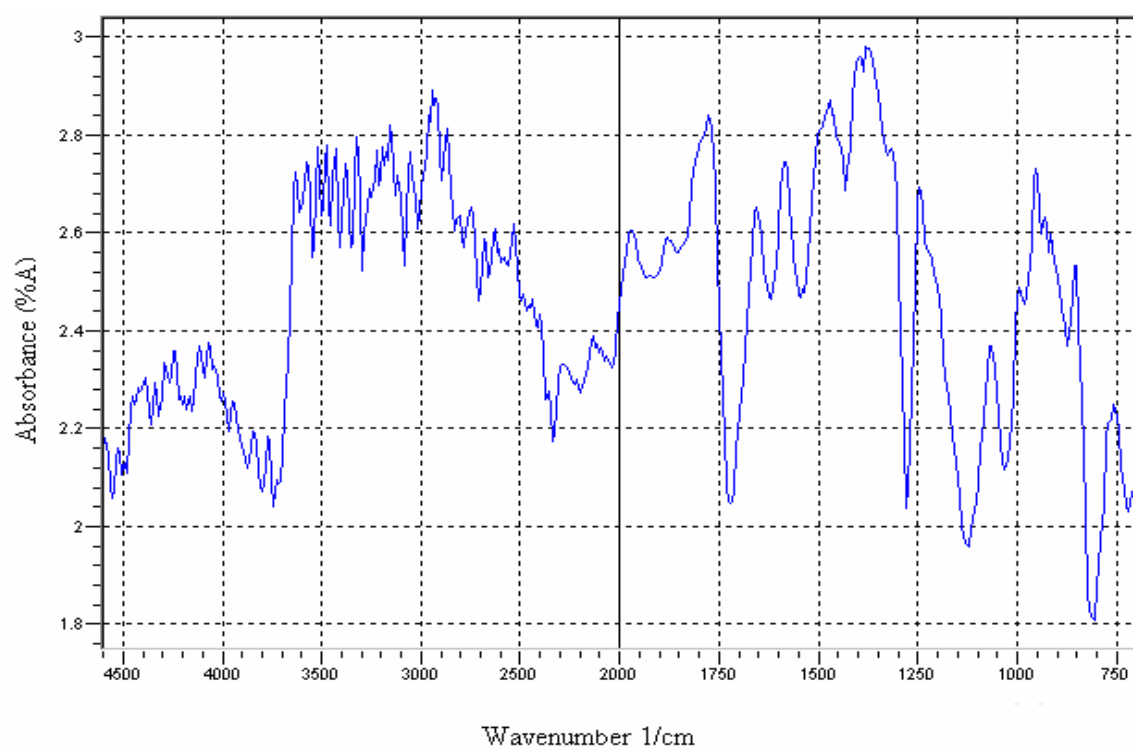
4.6.(g)



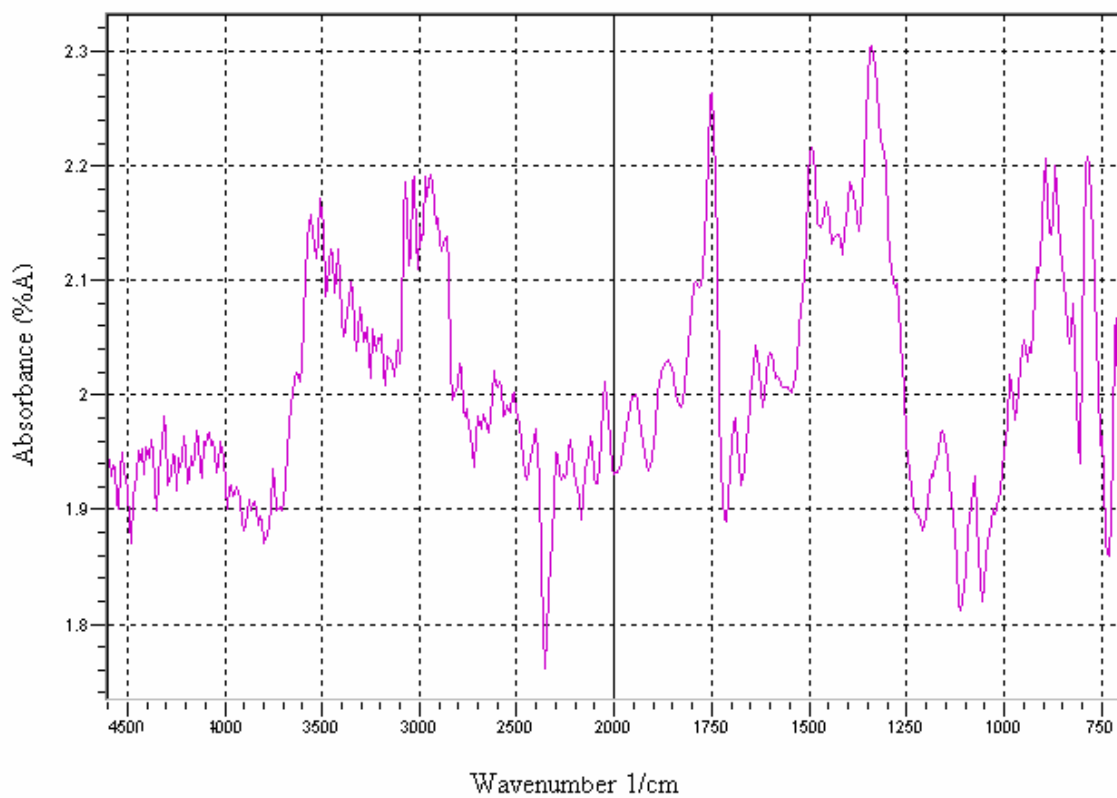
4.6.(h)



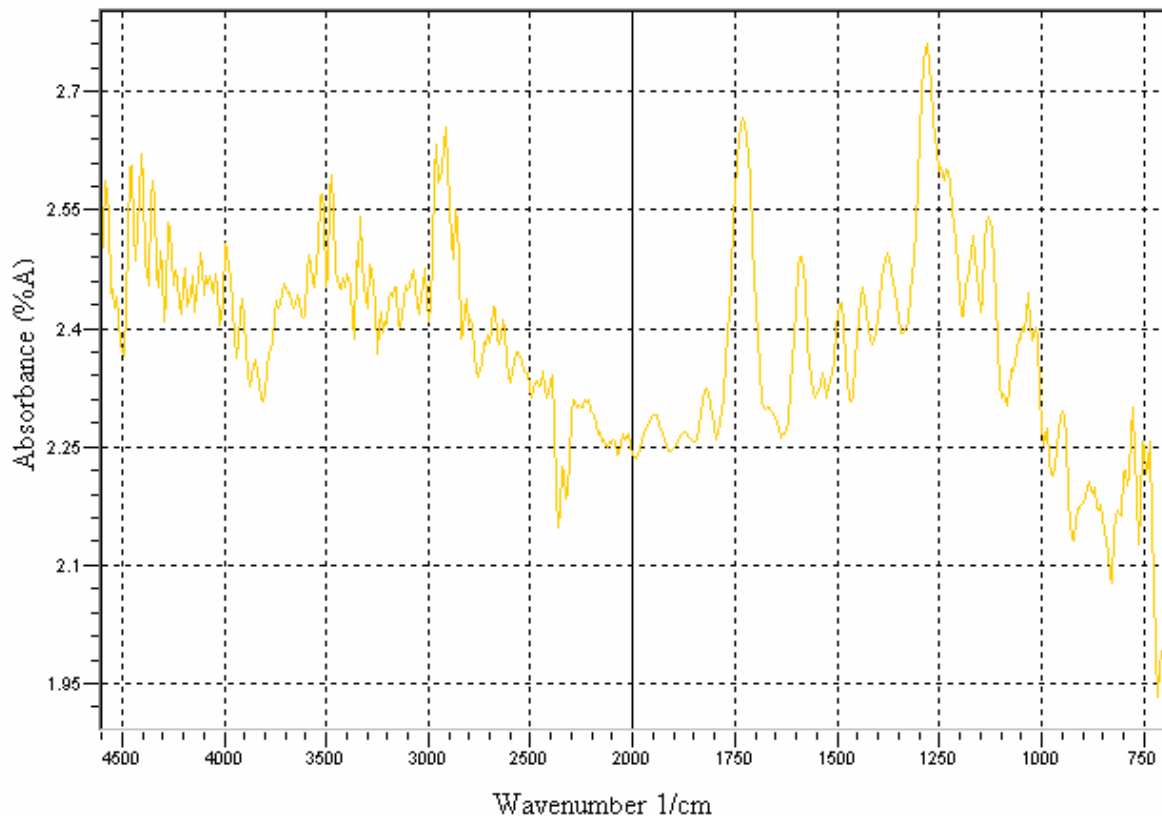
4.6.(i)



4.6.(j)



4.6.(k)

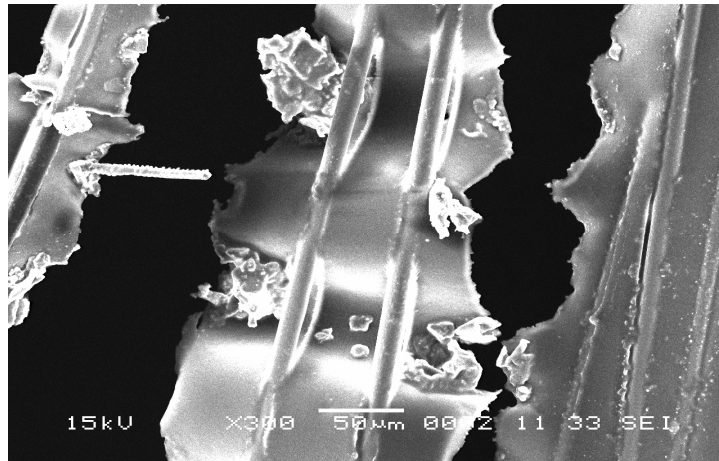


4.6.(l)

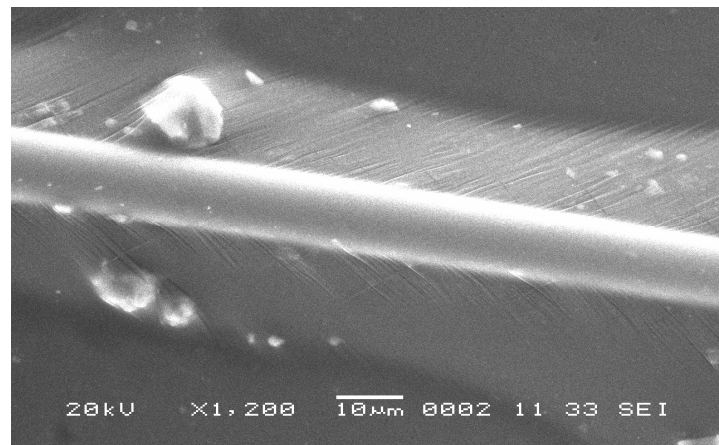
Fig.4.6. (a)-(f) The 2D micrograph taken by FTIR spectrophotometer, (g)-(l) there FTIR spectra for hydrothermally treated glass/polyester micro-composites at the interface for the treatment of 10-50 hours.

4.1.2.2. Microscopic interface analysis

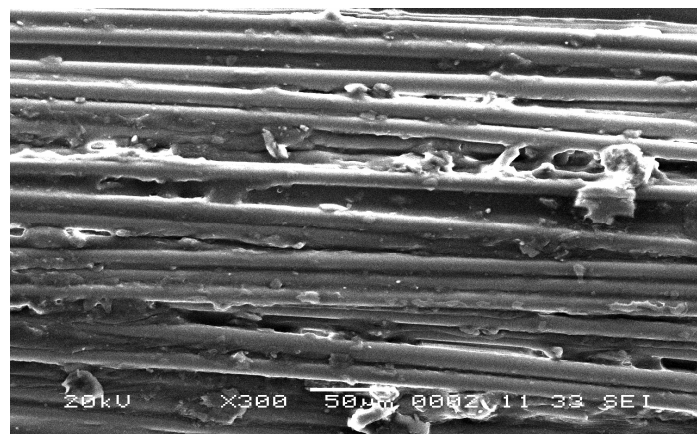
The SEM micrographs shows that the curing stresses were generated at the interface of the glass-polyester micro-composite due to difference in the coefficient of thermal expansion between them. The curing stresses generated at the interface can be relived by the moisture absorption or moisture absorption may results into swelling stresses at the interface. (Fig (4.7(b)) represents that after curing the polymer is not completely attached with fiber but form covalent bonds at some points (Fig4.7(a)). After the treatment these bonds were broken and hydrogen bonds were formed with better adhesion. The hygrothermal conditioning time was less it can only increase the interfacial adhesion by formation of strong hydrogen bond.



(a)



(b)



(c)

Figure 4.7 Scanning electron micrograph shows (a) polyester attached with glass fibre at some points in untreated glass/polyester micro-composite; (b) stress relaxation at the interface and better adhesion at the interface in aged glass/polyester due to moisture absorption micro-composites.

4.2. Cryogenic Treatment

In fibre reinforced plastics residual stresses are generated due to difference in CTEs (Coefficient of Thermal Expansion) between the matrix and the reinforcement which are relieved by physical process such as potholing, debonding at matrix/fibre interface, microcrackings etc. when they become large enough. The amount or density of microcrackings depends mainly on the tensile modulus of fibres and the matrix properties used in the composite. Addition of toughening agents in the matrix decreases the microcracking propensity of these laminates [39]. Complex stress patterns and numerous stress raisers arise in the matrix from a thermal mismatch with the glass fibres resulting in a variable and unpredictable failure pattern [53]. Residual stresses can be minimized by choosing the optimum ply angle [54] or by altering CTE of the matrix chemically to closer match the CTE of fibres. Some experiments reported improved mechanical properties of glass/epoxy laminates at low temperature [55]. Glass fibres and epoxy resins are known to be highly loading rate sensitive. The mechanical properties of glass reinforced epoxy composites are found to be rate sensitive even at low strain rates [56].

To study the loading rate sensitivity of polymeric composites at low temperature is of prime importance. CFRP structural components used in aircrafts can suffer high and low velocity impact at cryogenic temperature. Fibre reinforcement architecture and stacking sequence play an essential role in the behaviour of composites under such thermal and loading conditions [57]. In this work, the mechanical behaviour of chopped glass/epoxy composites were compared at cryogenic and at room temperature. DSC test was carried out to study whether there is any change in glass transition temperature after cryogenic treatment.

Figure 4.8 and figure 4.9 shows the effect of crosshead speeds on ILSS values at cryogenic temperature, ambient temperature after exposure to cryogenic temperature and at ambient temperature of untreated samples of chopped and woven glass/epoxy laminates. As chopped fibres provides more surface area than woven fibres, the amount of effective bonding with the available polymer matrix per unit surface area of the fibres will be less results in lower ILSS values than woven fibre composites. From figure 4.8 and figure 4.9 we note that the nature of the curve is different at above and below 50 mm/min crosshead speed. The ILSS value increases initially and decreases thereafter. The cryogenically conditioned laminates showed higher values than untreated laminates for both chopped and woven glass/epoxy composites. At lower strain rate the epoxy matrix is more ductile than the composite which may contribute to

lower ILSS values at lower crosshead speed. The matrix acts as the load transfer medium between the fibres, hence the performance of the composite depends on the capability of the matrix to transfer load through the interface. At lower speed there will be more deterioration in the matrix as more time is available for failure to take place results in lower ILSS values which increases with the crosshead speed [58]. At higher loading rates the reduction in ILSS values may be due to the restriction and minimization of relaxation process at the crack tip leading to the growth of stress induced cracks without blunting. The matrix is unable to transfer the load properly due to less availability of time at higher speed i.e. the load on the matrix is like an impact. Several damage mechanisms may appear such as fibre fracture, matrix cracking, fibre pull-out and delamination. Hence it can be concluded that the laminate requires an optimum time to transfer load effectively through the interface.

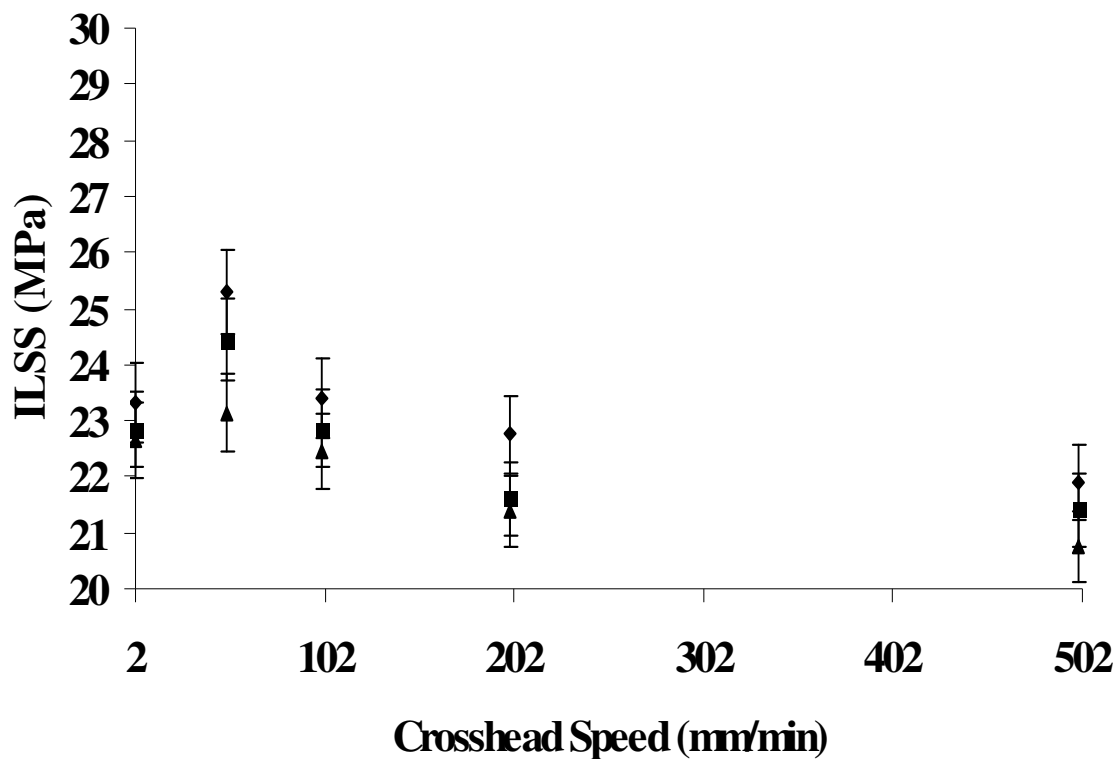


Fig.4.8. Variation of ILSS of chopped glass-epoxy composites with crosshead speed at cryogenic temperature (◆), ambient temperature after cryogenic conditioning (■) and ambient temperature (▲).

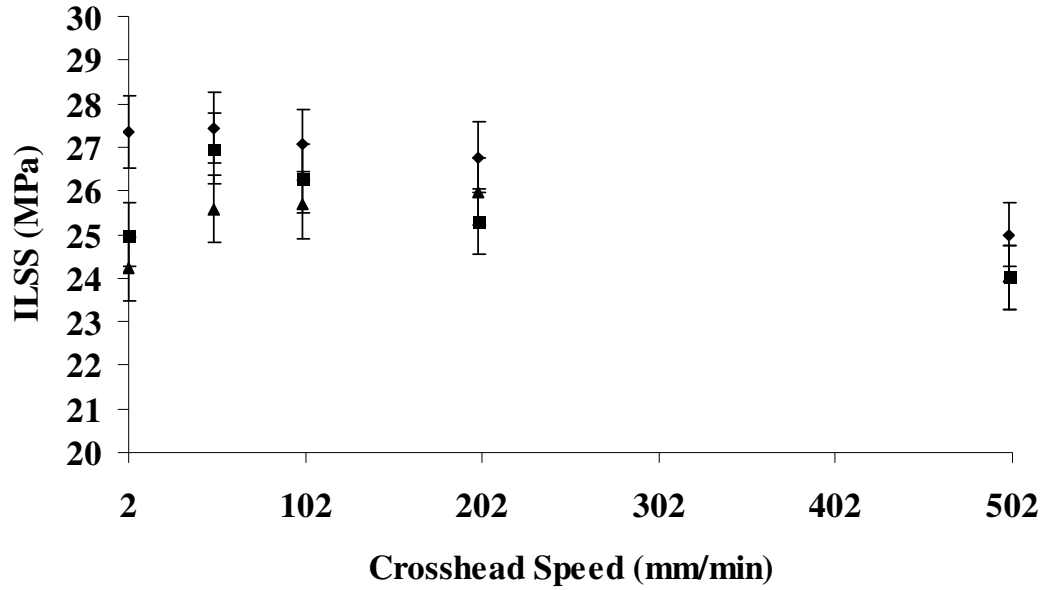


Fig. 4.9. Variation of ILSS of woven glass-epoxy composites with crosshead speed at cryogenic temperature (◆), ambient temperature after cryogenic conditioning (■) and ambient temperature (▲).

The conditioning at cryogenic temperature may result in cryogenic hardening of the epoxy matrix. There may be generation of microcracks in the matrix due to thermal shock. These can be avoided by slowly decreasing the temperature from room temperature. The ILSS reflects the resistance of a layered composite material to forces that tend to induce a relative motion between the layers parallel to them. Thus, the sign of improvement in the shear value after cryogenic conditioning is probably due to differential thermal contraction (figure 4.10 and figure 4.11) of the matrix during sudden cooling which leads to the development of greater cryogenic compressive stresses and may increase the resistance to debonding and better adhesion by mechanical keying factor at the interface between fiber and the matrix [59,60]. The rise in ILSS value may be attributed to the improved adhesion by cryogenic conditioning and also by the post-curing strengthening phenomena [10]. The cryogenic hardening was found to be one of the prominent factors responsible for enhancement in wear performance of composites [61]. It was observed that more amount of matrix residue adhered (figure 4.12) to the fibre for cryogenically conditioned specimens. This may be due to increase in friction and adhesion between fibre-matrix depending on the compression by contraction of matrix as the polymer contracts more than the glass.

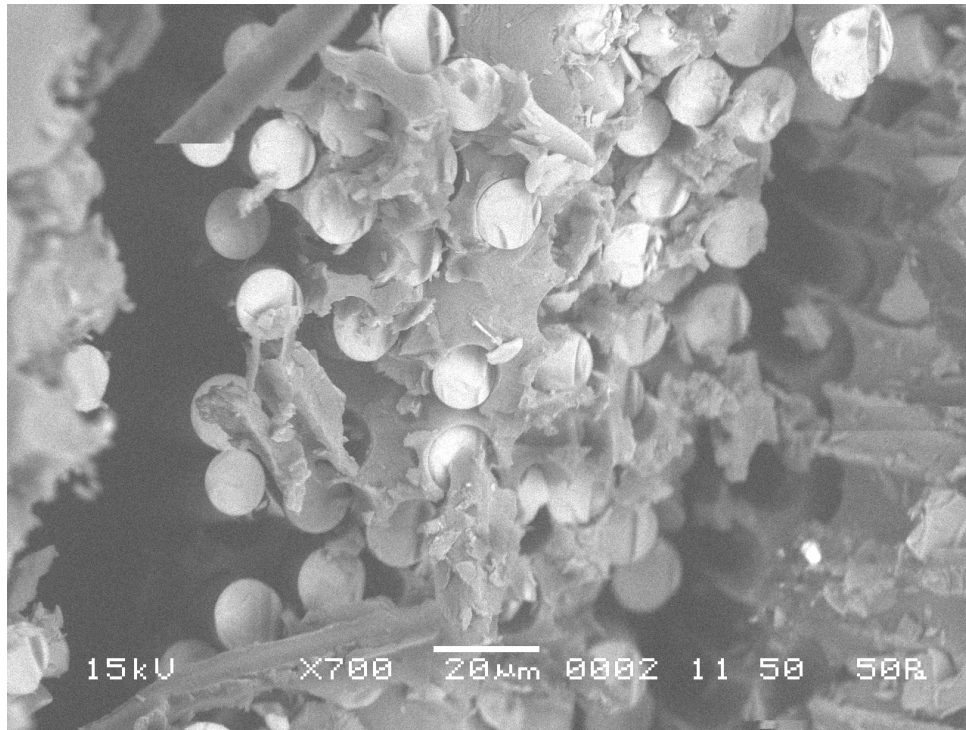


Fig.4.10. Scanning micrograph shows no contraction of epoxy matrix of as cured specimen at ambient temperature.

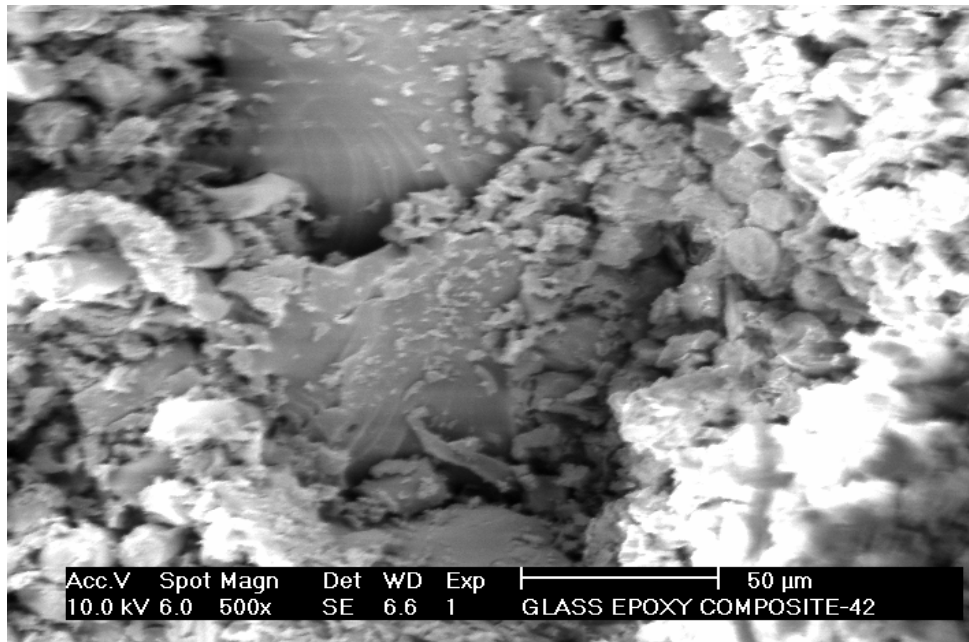


Fig.4.11. Scanning micrograph shows contraction of epoxy matrix of cryogenically conditioned specimen.

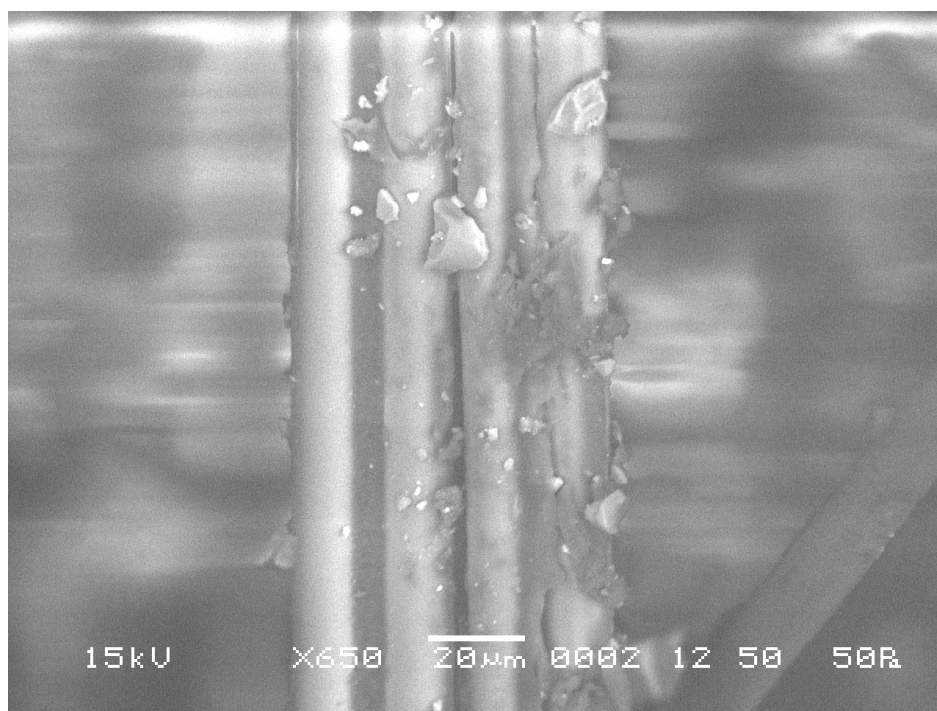


Fig.4.12. Scanning micrograph shows matrix residue adhered to the fibre for cryogenically conditioned specimen.

Failure of the matrix occurs when the stresses greater than the shear strength of the matrix is readily generated. The specimens tested at room temperature after cryogenic conditioning showed lower ILSS values but higher than the untreated specimens. This may be due the relaxation of the compressive stresses generated when cryogenically conditioned.

Figure 4.13 shows the comparison of glass transition temperature (T_g) of the chopped glass/epoxy laminates of untreated and cryogenically conditioned specimens. There is an increase in T_g after the cryogenic conditioning. Cryogenic conditioning causes freezing of the polymeric molecular chains that restricts motions at low temperature. Here both the motions segmental motion and the total mobility of the molecule as a whole are frozen and the molecular mobility is arrested causing decrease in chain flexibility. The increase in glass transition temperature (T_g) is due to incomplete reversibility of molecular chain mobility. Cryogenic conditioning can be considered as a treatment which makes the microstructure of the composite more orderly. It was reported that damping behaviour of glass/epoxy composites at low temperature is irreversible that is the phase transition because of the temperature change is not always reversible [59]. In case of thermoplastics the degree of crystallinity has increased after the cryogenic treatment which results in marginal increase in glass transition temperature [45].

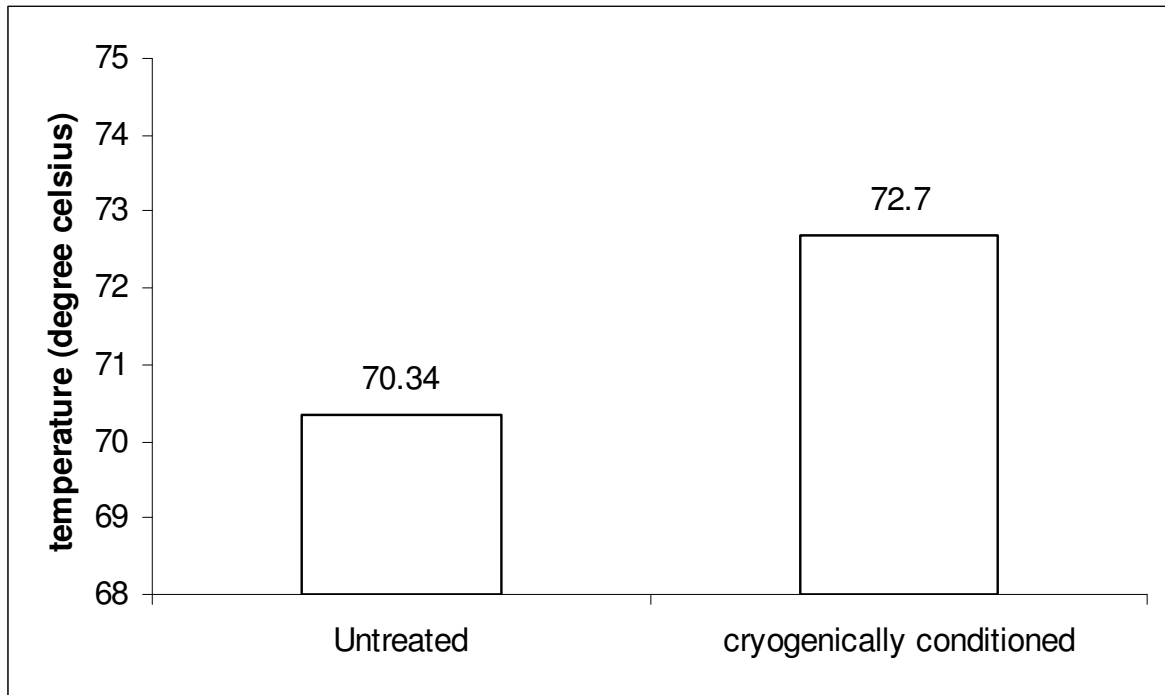


Fig.4.13. Bar chart showing variation of glass transition temperature after cryogenic conditioning of the laminate.

5. CONCLUSION

5.1. Hygrothermal treatment

In the present work, hygrothermal treatment of bisphenol-A based epoxy resin and unsaturated polyester resin reinforced with glass were monitored. The results of FTIR-imaging and DSC suggest that there is a variation in the chemical behavior after hygrothermal conditioning. The increase of OH absorbance intensity in the FTIR spectra shows that curing is fast in the bulk region in comparison to fibre/matrix interface. The moisture sorption at the interface by the matrix phase is a very complex phenomenon due to different absorption at the interface i.e. water molecule forms strong hydrogen bond with the epoxy resin and polyester resin or less strongly bonded hydrogen bond. Due to moisture absorption peaks get widen and intensity increases at 3610 cm^{-1} . This shows that it that hygrothermal conditioning leads to change in the spectra at the interface and bulk, but the interface is more affected due to its heterogeneous nature. If the structure near the interface changes the stress transfer from the matrix to the fibre will change and ultimately the overall performance of FRP composite will be change. T_g also increased in the initial stages of ageing. This may be due to the double bond formation in the matrix or reduced flaw size due to the plasticization. This suggests that FTIR-imaging and DSC techniques may solve the problem of physio-chemical analysis of interface of composites.

5.2. Cryogenic Treatment

It can be concluded that the ILSS values for chopped fibre composites are found to be lower than woven fibre composites. This can be due to less amount of effective bonding with the available polymer matrix per unit surface area of the fibres. The higher ILSS values for cryogenically conditioned samples is attributed to enhanced mechanical keying factor by the generation of cryogenic compressive stresses The composites laminate needs an optimum time to transfer load effectively through the interface. We marked an increase in glass transition

temperature after cryogenic conditioning of the laminates which may be due incomplete reversibility of molecular chain mobility resulting in reduced chain flexibility.

5.3. Scope for Future Work

The present work leaves a wide scope for future investigators to explore many other aspects of physio-chemical analysis of interface of FRP composites. Study of complex moisture diffusion mechanism into the epoxy and polyester resin may help in the evaluation of interface of FRP composites. The moisture present in the matrix in the free form or/and combined form and which phase come first is still a matter of discussion, this may help be evaluation by spectra shift by FTIR-imaging and DSC techniques. A small work has done here to identify this behaviour up to some extent.

The present work also leaves a scope for effect of low temperature on the T_g of the FRP composites. The study of freezing of chain flexibility at low temperature and its effect on T_g is a not explained in the literature available.

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